THE ROLE OF BACTERIA IN THE DEPOSITION AND EARLY DIAGENESIS OF THE POSIDONIENSCHIEFER, A JURASSIC OIL SHALE IN SOUTHERN GERMANY

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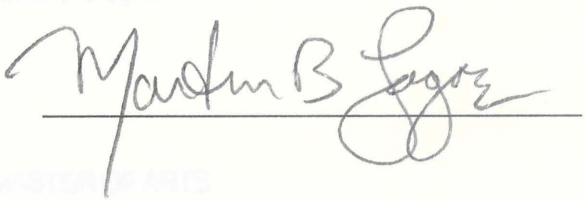

THE ROLE OF BACTERIA IN THE DEPOSITION AND EARLY DIAGENESIS OF THE POSIDONIENSCHIEFER, A JURASSIC OIL SHALE IN SOUTHERN GERMANY

by

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Franz K. Hiebert
Austin, Texas
April 20, 1988

ABSTRACT

The Jurassic (Toarcian) Posidonienschiefer of southern Germany is famous for its well preserved vertebrate fossils and its high organic content. The majority of the Posidonienschiefer (10 meters thick in the study area) consists of the Bituminous Shale, a fossiliferous laminated illite claystone. Two thin (30-40 mm) clayey pyritic biomicrosparites, the Upper and Lower Schlacken, interrupt the Bituminous Shale. Geologists who have studied the Posidonienschiefer disagree about the exact nature of its depositional environment. The argument centers on the interpretation of an impoverished benthic fauna and whether or not the water column directly above the sediment-water interface was anoxic or normally oxygenated. Kauffman (1981) proposed that an algal/fungal mat located at or near the sediment/water interface marked the boundary between aerobic and anaerobic conditions during deposition. The purpose of my research was to investigate the geologic conditions during deposition and early diagenesis of the Bituminous Shale and the Schlacken and to search for evidence of microbial activity. A detailed petrologic investigation of these two lithologies found no evidence of an algal/fungal mat, but did reveal the important contribution of microbial activity in the formation of pyrite and calcite cement.

The Bituminous Shale was deposited in a low-energy tropical seaway. The upper water-column supported a diverse marine fauna. The aerobic/anaerobic boundary in the water column may have been located several millimeters above the sediment/water interface. Pore waters of the ocean-floor mud were dysaerobic to

anaerobic. Occasional oxygenation events allowed opportunistic benthic organisms to colonize the sea-floor.

Compaction of the Bituminous Shale occured prior to cementation of original porosity. Framboidal pyrite was formed during sulfidic diagenesis under anaerobic, but open, sediment/pore water conditions. Euhedral pyrite formed later as communication between pores became restricted during sediment compaction.

The skeletal grains of the Schlacken formed as a winnowed lag deposit of Bituminous Shale sediment. During the early stages of sulfidic diagenesis the winnowed beds were rapidly cemented in a concretion-like sheet. Early cementation preserved delicate algal spores and clay fabric.

Fossil bacteria were discovered in the calcite cement of the Schlacken by modified petrographic techniques, and confirmed with the scanning electron microscope. Experiments in which live bacteria were gradually entrapped in halite produced a crystal fabric identical to that of the fossiliferous calcite cement of the Schlacken.

The microbial production of bicarbonate and ammonia during sulfidic diagenesis played a significant role in altering local geochemical conditions in the Schlacken sediment and initiated the precipitation of calcite cements. Fossil bacteria in the cements of the Schlacken are direct evidence of the presence and entrapment of bacteria during cementation, but do not conclusively prove their active role in the formation of calcite.

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Introduction

The study of geomicrobiology and sedimentation as an integrated system represents a new approach to understanding the deposition and early diagenesis of organic-rich shales. Bacteria are fundamental recyclers of organic matter; they break down complex biosynthesized molecules into simple chemical building blocks such as oxygen, hydrogen, nitrogen, sulfur, and carbon. In the marine realm, detritus-degrading bacteria are concentrated and mingled with sediment at the sea floor in concentrations of up to 10^6 bacteria per cubic centimeter. A large literature exists describing both marine microbiology and diagenesis of organic-rich sediments, but little effort has been made to combine these closely related subjects. This thesis investigates two lithologies of the Posidonienschiefer, an oil-shale from the Jurassic of southern Germany. Fossils and geochemical constituents indicate that bacteria played an important role in the deposition and early diagenesis of this shale.

The Posidonienschiefer is famous for its magnificently preserved vertebrate fossils and for its high percentage (2-18%) of preserved organic matter (Kuspert, 1982, Moldowan *et al.*, 1985). Over the past ten years the paleontological literature has served as a stage for a debate about what environment must have prevailed during the deposition of the Posidonienschiefer. The argument centers on the interpretation of an impoverished benthic fauna and whether or not the water column directly above the sediment-water interface (SWI) was anoxic or normally oxygenated.

Erle Kauffman's paleoecological study (1981) of the Posidonienschiefer combined with ideas from current research at the University of Texas into the role of bacteria in the formation of carbonate cements inspired a re-examination of the Posidonienschiefer to determine if microbial processes might have contributed to the formation of this shale. This thesis research combines a petrographic study of fabric with an analysis of the diagenetic constituents of two distinct lithologies within the Posidonienschiefer to address the question of what was happening at and near the sediment-water interface during deposition and early diagenesis.

This thesis has two main results : 1) to report the discovery of one of the few known occurrences of fossil bacteria in a carbonate cement, and 2) to propose a microbial mechanism for creating geochemical conditions during early diagenesis that promote the production of pyrite and carbonate cement.

In addition, I hope this work emphasizes the importance of studying microbial activity and sedimentation as a single system in order to understand the formation of organic-rich rocks.

Study Location

Samples of the Posidonienschiefer for this study come from two quarries in the Toarcian (Liassic) outcrop belt of the Swabian Alps in Southwestern Germany (Figure 1). One quarry located in Dotternhausen is owned by a cement company which burns the organic-rich shale for energy and uses the residual slag as base material for cement manufacture. The Hauff quarry (Figure 2), located near Holzmaden, is the site from which many museums have obtained exquisitely preserved and prepared fossils of *Seirocrinus*, the giant driftwood-hosted crinoid, as

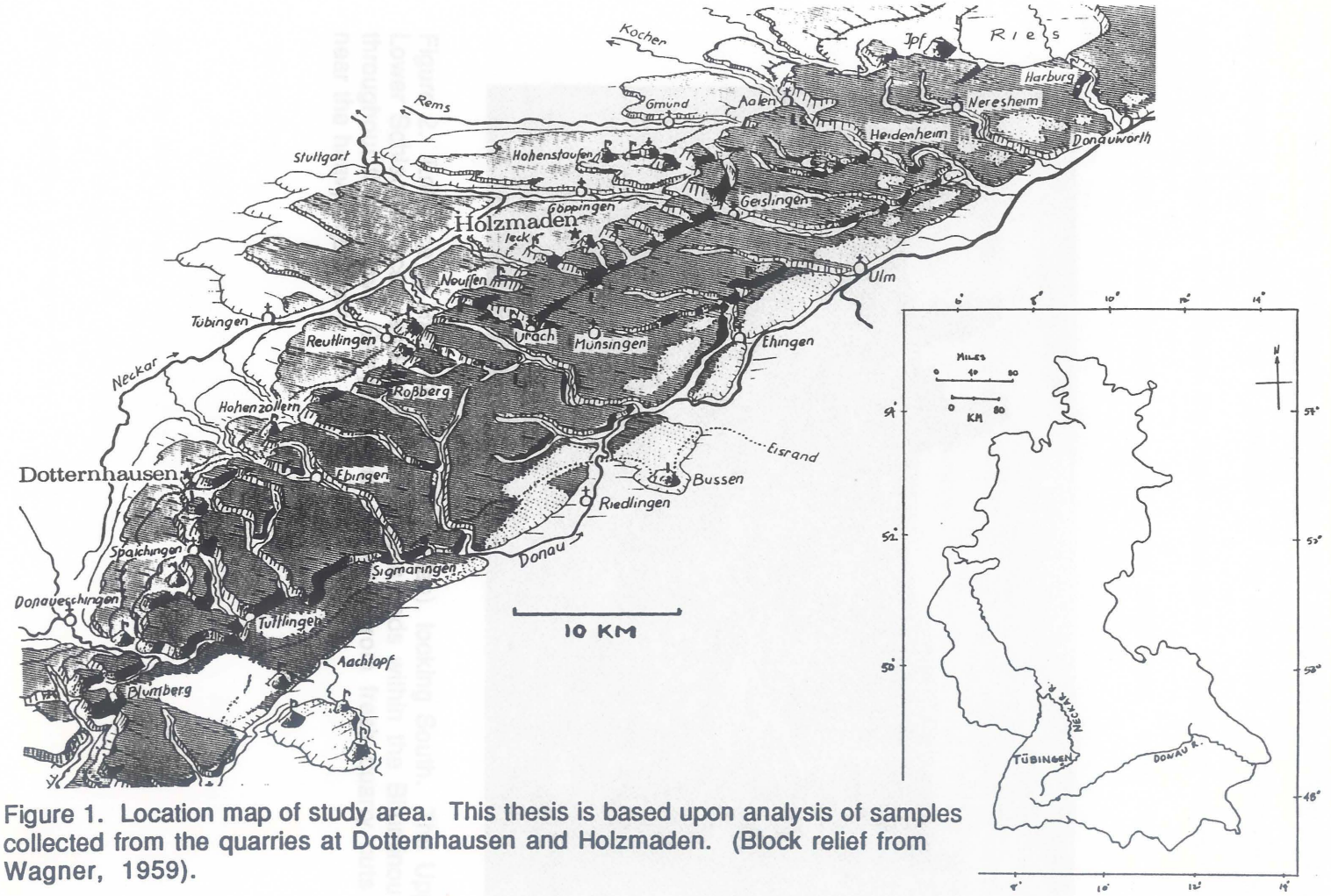


Figure 1. Location map of study area. This thesis is based upon analysis of samples collected from the quarries at Dotternhausen and Holzmaden. (Block relief from Wagner, 1959).

Figure 2. Entrance to Hauff Quarry (Holzmaden), looking South. The Upper and Lower Schlacken occur as laterally continuous beds within the Bituminous Shale throughout this quarry. Samples were collected from fresh quarry cuts located near the heavy equipment.

well as ichthyosaurs, plesiosaurs, crocodiles, and many types of fish (Hauff, 1981). Rolf Bernard Hauff, trained as a geologist at the University of Tübingen, owns and manages the quarry and directs the Hauff Museum in Holzmaden where magnificent examples of the Posidonienschiefer fauna are displayed. Herr Hauff graciously allowed me to work in his quarry, guided me to the best collecting areas, and even had his quarrymen cut fresh exposures for collection of unweathered samples.

Regional Geology and Paleogeography

During Toarcian time (≈184 Million Years Ago (MYA)) the continents were grouped into two major supercontinents, Gondwanaland in the Southern Hemisphere and Laurasia in the Northern Hemisphere. The North Atlantic Ocean was just beginning to open. The super-continents were divided by the Tethys seaway which straddled the equator between 30°N and 35°S latitude.

The confluence of the southern Arctic Ocean and the northern margin of Tethys extended across what is now southern Europe and the Posidonienschiefer study area. Ziegler (1982) has reconstructed the paleogeography of central Europe during Lower Jurassic time. The Posidonienschiefer depositional area was located about 100 kilometers northwest of the Bohemian Massif (= Böhmisches Land of Figure 3).

Hallam (1975, 1978) has proposed that the Jurassic epicontinental seas which covered Europe were largely shallow (maximum depth of 15 to 30 meters) with extremely gradual seaward-sloping ocean floors. Ammonite fossils preserved in a vertical orientation in the Posidonienschiefer suggest that the total water depth was less than 30M (Raup, 1973). Such an ocean geometry would have the effect of depressing tidal ranges and wave energy upon shorefall, thus promoting the development of a quiet, or stagnant water column.

An equitable tropical climate stretched across the equatorial belt from 63°S to 75°N latitude throughout the Jurassic (Hallam, 1975). Lack of polar ice caps had the effect of smoothing-out global temp-erature variations and thus slowing major atmospheric and oceanic circulation. Tropical plant fossils,

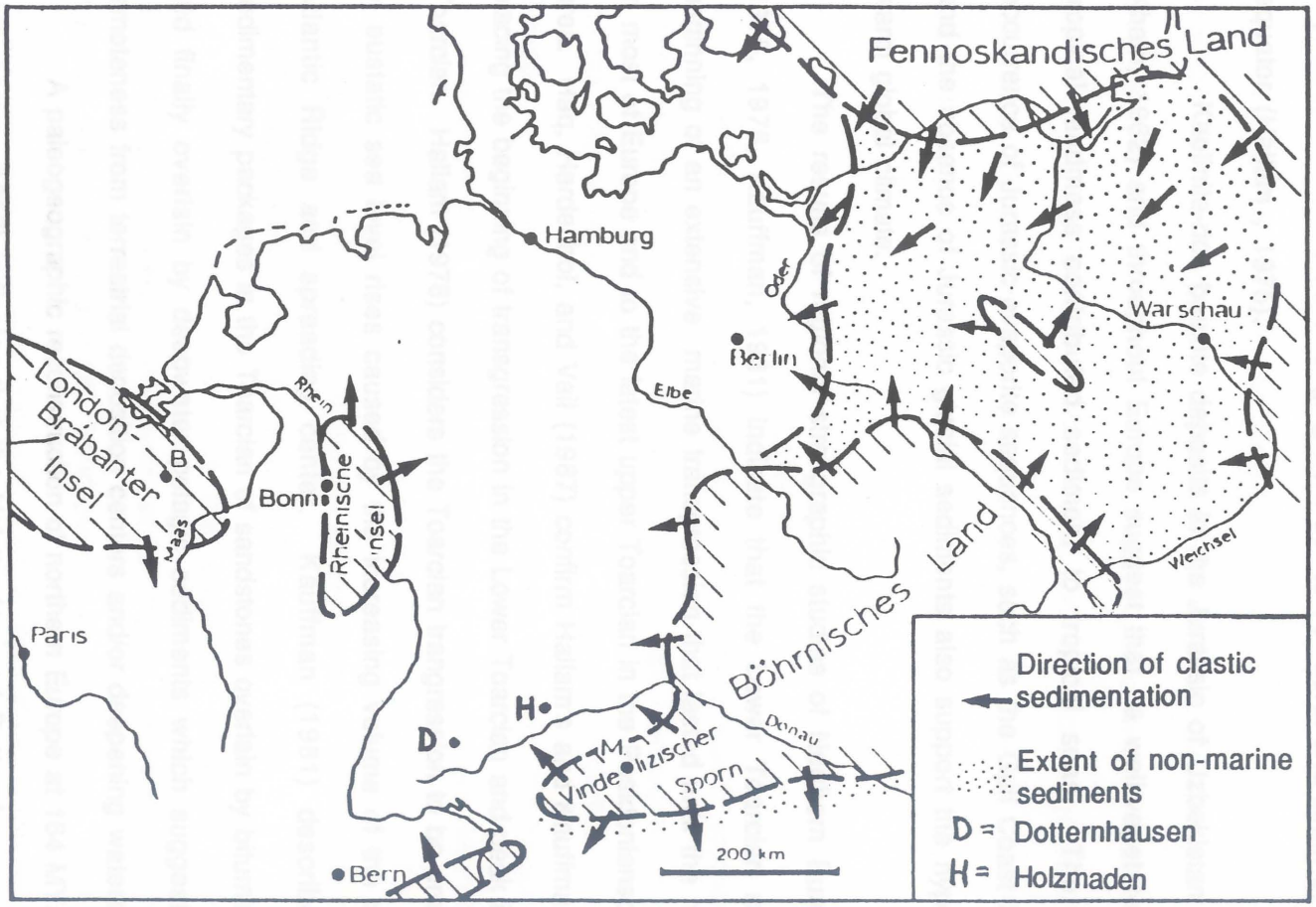


Figure 3. Paleogeography of Central Europe during the Lower Jurassic indicating the location of Dotternhausen and Holzmaden in relation to the Bohemian Massif (= Böhmisches Land). (Figure after Ziegler, 1982).

extensive coal deposits and coral reefs are preserved in rocks which were deposited in a broad band ranging from 60° to 75° north and south of the Jurassic equator (Hallam , 1975).

Kaolinite-rich bauxite deposits in the Jurassic of Uzbekistan (Ronov and Khain, 1962) and throughout Europe suggest that a well-vegetated, low-relief tropical landmass contributed sediment to tropical seas. The widespread occurrence of Jurassic evaporite sequences, such as the Gulf Coast Louann Salt, and the absence of Jurassic glacial sediments also support the hypothesis of a warm global climate.

The results of regional stratigraphic studies of Northern Europe (Hallam 1975, 1978, Kauffman, 1981) indicate that the Lower Toarcian marked the beginning of an extensive marine transgression that lasted until the mid-Toarcian in most of Europe and to the latest upper Toarcian in the Posidonienschiefer study area. Haq, Hardenbol, and Vail (1987) confirm Hallam's and Kauffman's findings, placing the beginning of transgression in the Lower Toarcian and peak in the Upper Toarcian. Hallam (1978) considers the Toarcian trangression to be one of a series of eustatic sea level rises caused by the increasing volume of the active North Atlantic Ridge and spreading center. Kauffman (1981) describes regional sedimentary packages in the Toarcian of sandstones overlain by bituminous shales and finally overlain by deepwater pelagic sediments which suggest increasing remoteness from terrestrial deposition centers and/or deepening waters.

A paleogeographic reconstruction of northern Europe at 184 MYA (M. Ross, pers. comm., 1987) indicates that the Holzmaden and Dotternhausen localities of

the Posidonienschiefer were deposited at approximately 28°N latitude, 38°E longitude.

The paleogeography of Jurassic northern Europe that has been inferred from the above findings is consistent with a climate of global equanimity. Low-relief land masses are suggested by the wide-spread predominance of very fine-grained clastic marine rocks. Plant fossils such as *Ginko digitata, Pagiophyllum kurri,* and *Otosamites mandelslohi* (beautifully illustrated in Hauff, 1981) indicate that the land was covered by tropical vegetation or inundated by swamps.

Local Geology

The Posidonienschiefer crops out in the Swabian Alps of southern Germany, east of the Rhein Graben, and north of the Swiss Alps (see location map, Figure 1, and the map of regional geology, Figure 4). This unit underlies much of central Europe. In addition to the outcrops in southern Germany, the Posidonienschiefer (or its equivalent) is found from the surface to 2500 meters depth in the Paris basin, where it provides the source of oil production in the city of Paris (Tissot *et al.*, 1971) and crops out again along the eastern shore of England in Yorkshire as the Jet Rock Shales (Moldowan *et al.*, 1985, Hallam, 1975).

Maximum burial depth of the shale in southern Germany was approximately 500 meters (Moldowan *et al.*, 1985). No metamorphic minerals or fabrics were observed in any hand samples or thin sections. The quarry faces reveal horizontally continuous beds with a slight regional dip to the SE. A regional

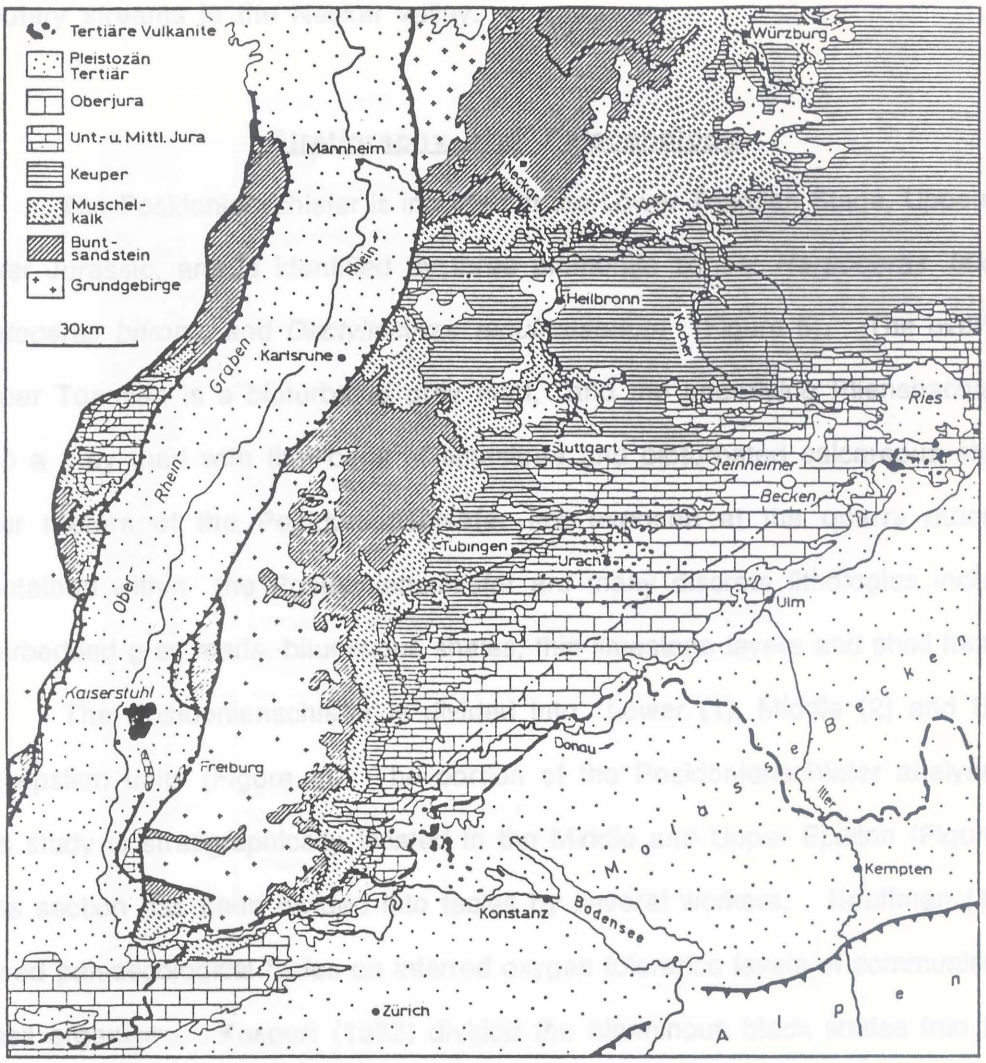


Figure 4. Geology of South-west Germany. (Figure from Geyer and Gwinner, 1986.)

system of NW and NE trending fractures is evident from drainage patterns of tributary streams in the Neckar valley.

Stratigraphy and Paleoecology

The Posidonienschiefer is included in the Lower Toarcian Stage, Uppermost lower Jurassic, and is identified by three ammonite zones: *Harpoceras falcifer, Hildoceras bifrons,* and *Dactylioceras tenui-costatum* (Figure 5). The overlying Upper Toarcian is a bioturbated grey marl, and the underlying Pliensbachian is also a grey marl with thin beds of limestone and bioturbated calcareous shales. Four meters of the Posidonienschiefer are exposed at the quarry outcrops. Contained within the Posidonienschiefer are many discrete lithologies including interbedded gray marls, bituminous shales, thin limestone layers and shell hashes.

The Posidonienschiefer is divided into Lower (1), Middle (2) and Upper (3) epsilon units (Figure 5). The portion of the Posidonienschiefer analysed in this study is stratigraphically located in the Middle and Upper Epsilon (Figure 6). This section has been divided into facies by several workers. Kauffman (1981) based paleoecological facies on inferred oxygen tolerance levels of communities of fossil organisms. Kuspert (1982) divided the bituminous black shales into three facies based upon stable ^{13}C isotope characteristics of carbonate and kerogen (Figure 7). Carbonate and kerogen in Facies A are depleted in ^{13}C. Facies B is relatively enriched in ^{13}C compared to A, and Facies C has ^{13}C values that range between those in A and B (see Review of Previous Geochemical Research section for details). This study focuses on the interval from the upper 100 cm of Facies B, through the lower 400 cm of Facies C (Figure 6). The two major lithologies

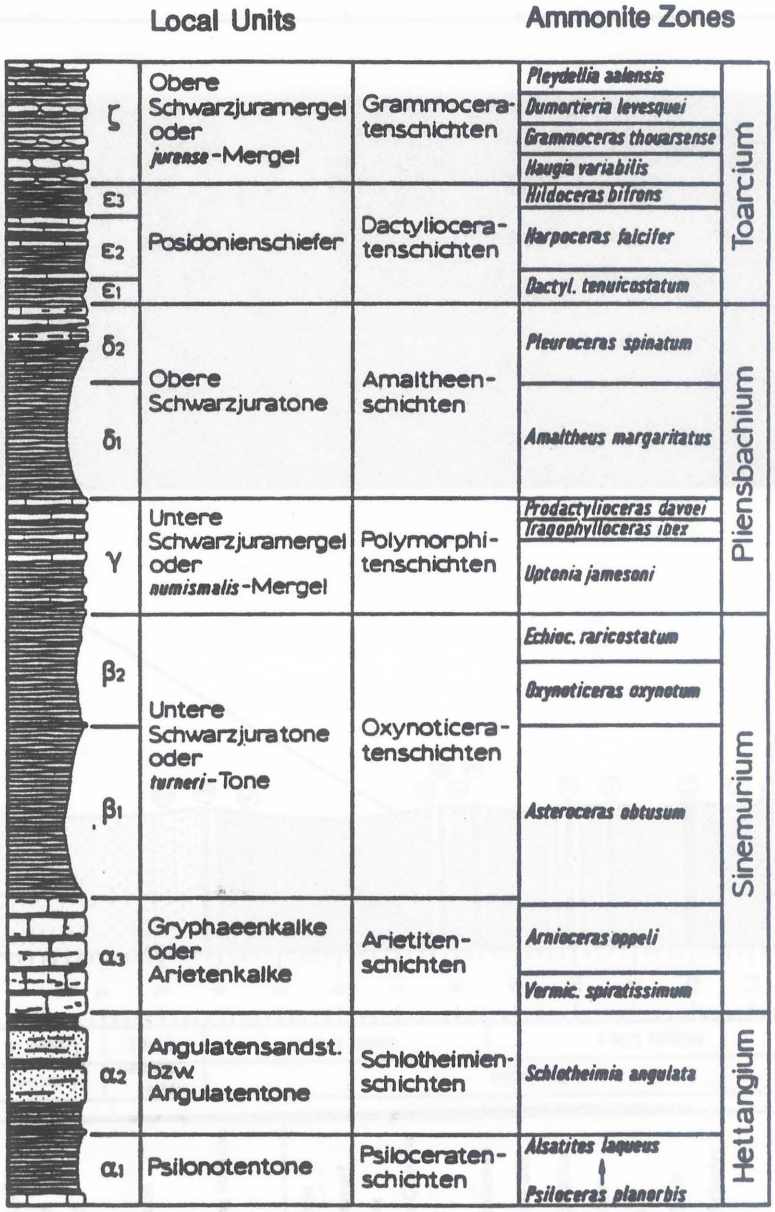


Figure 5. Stratigraphic column of the Jurassic rocks in South-west Germany. (Modified after Geyer and Gwinner, 1986.)

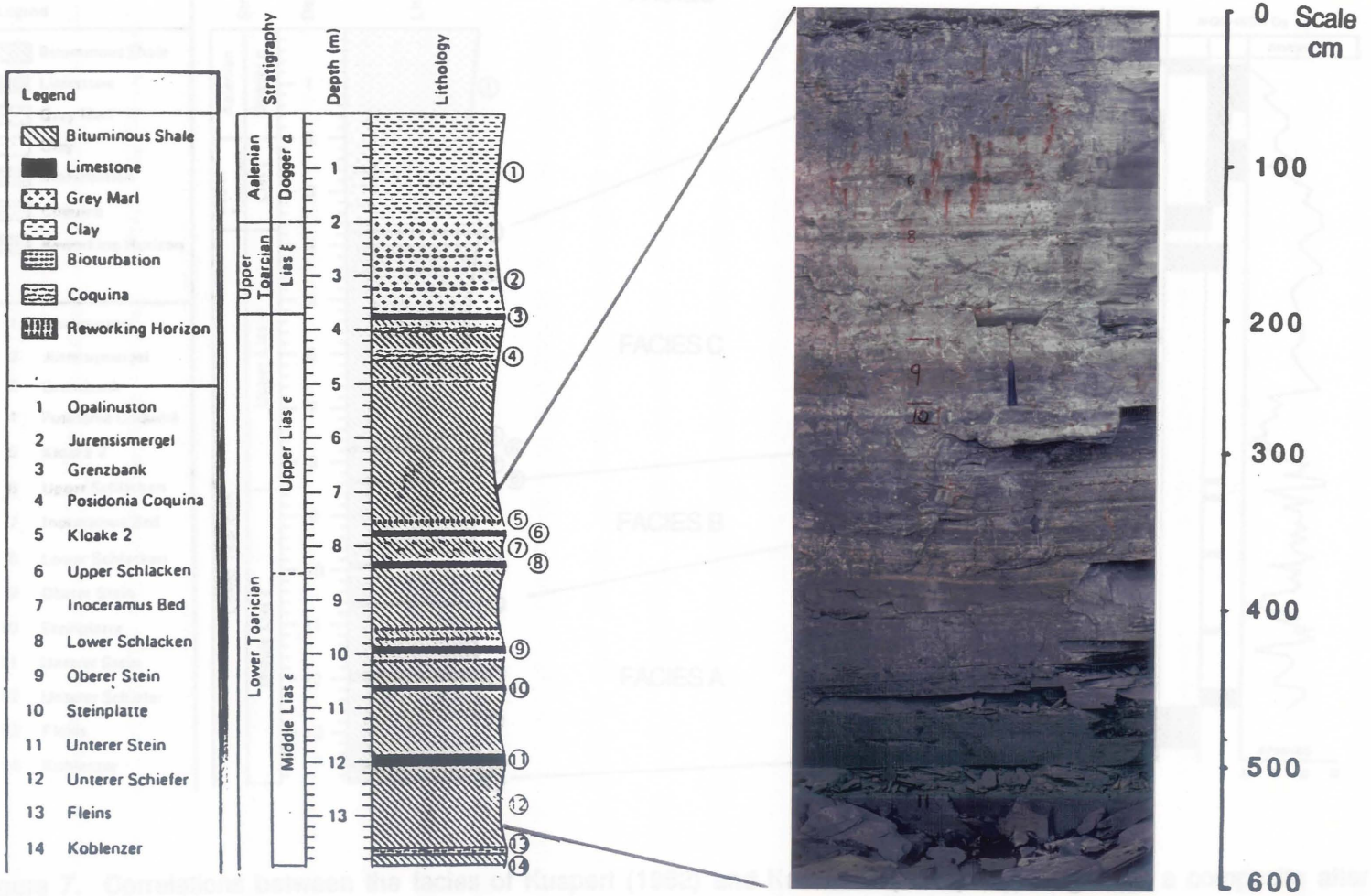


Figure 6. Stratigraphic column of the the Posidonienschiefer and portion of the Hauff Quarry outcrop studied in this thesis. Numbers on the outcrop correlate to the stratigraphic column key. (Modified after Moldowan et al., 1985).

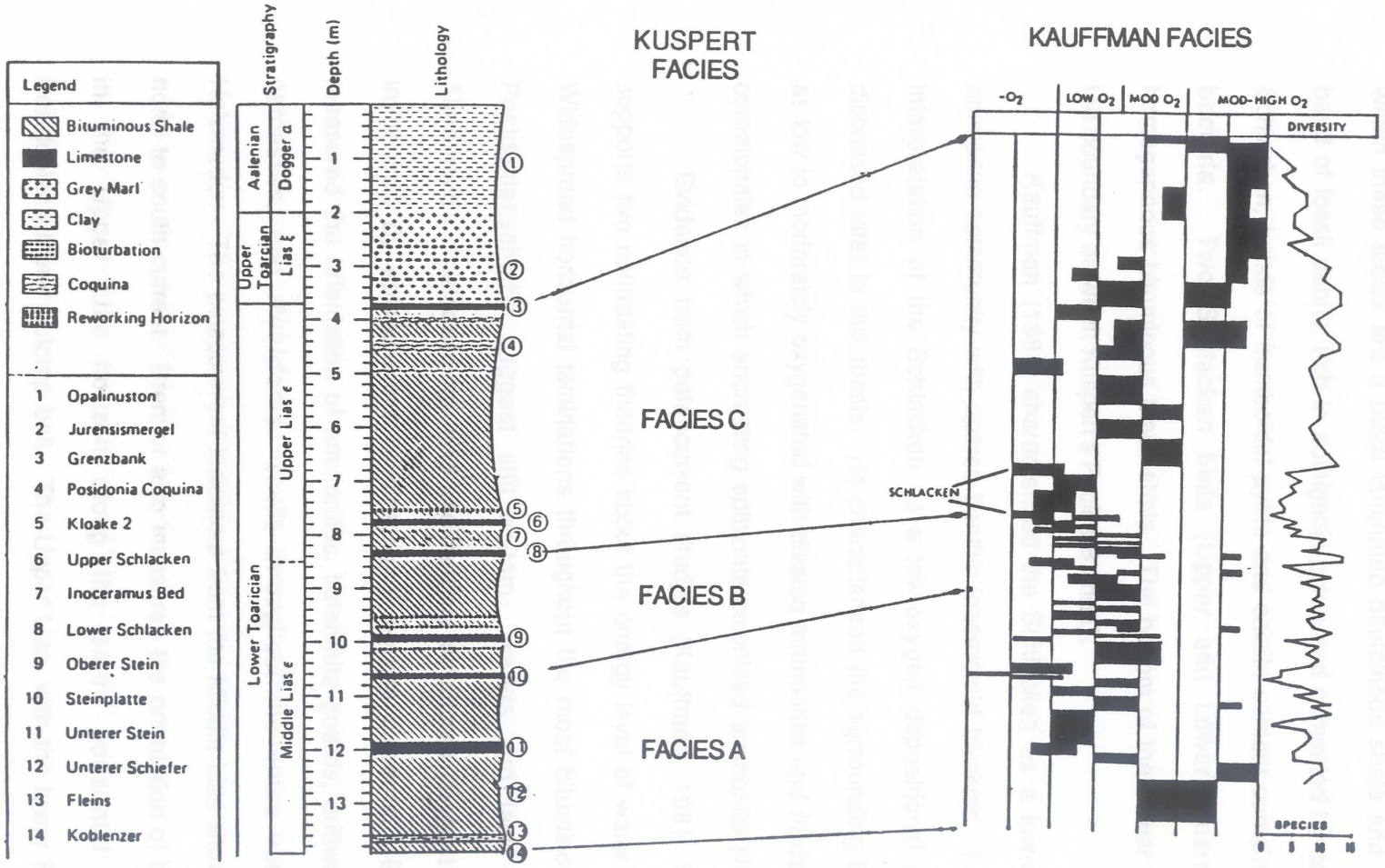


Figure 7. Correlations between the facies of Kuspert (1982) and Kauffman (1981). This figure is a composite after Moldowan et al. (1985) and Kauffman (1981).

within these facies are a black laminated bituminous shale and the Schlacken, a band of fossil debris, rich in authigenic pyrite and cemented by calcite. Within the Schlacken, bands of framboidal pyrite and calcite cement contain numerous fossil bacteria. Two Schlacken beds (Upper and Lower) interrupt the largely homogeneous bituminous black shale. The bottom of the Lower Schlacken marks the boundary between Kuspert's Facies B and C.

Kauffman (1981) characterized the Schlacken as a low-oxygen tolerating ammonite community with sparse benthic inoceramid bivalves. I disagree with his interpretation of the Schlacken as a low-oxygen depositional event as will be discussed later in this thesis. He characterized the surrounding Bituminous Shale as low to moderately oxygenated with diverse ammonites and *Inoceramus* biostrome communities in which encrusting epibionts colonized ammonite shells.

Evidence from paleocurrent studies (Kauffman, 1981, Seilacher, 1985) supports two contrasting theories about the energy level of water at the sea floor. Widespread horizontal laminations throughout the most bituminous shales of the Posidonienschiefer suggest still bottom waters and lack of bioturbation. Alternatively, paleoecology and sedimentary structures suggest an environment influenced by episodic but unidirectional bottom currents. Brenner (1977a) measured the orientation of ammonites, belemnite guards, driftwood, ichthyosaur carcasses, and *Posidonia* shells throughout the entire vertical section at Holzmaden. The paleocurrent indicators from the Middle Lias showed a consistent north to south current. Brenner also measured the orientation of belemnite guards in the Upper Lias horizon along the entire horizontal extent of the Posidonienschiefer outcrop belt. The Upper Lias, with the lower Schlacken at the

base, indicates an abrupt and long term change in current direction from SSE to NNW (Figure 8, Brenner and Seilacher, 1978). Seilacher (1982) states that Brenner's paleocurrent evidence indicates that the episodic currents had a velocity of up to 20 cm/second, but does not report the method for determining this flow.

The fossil fauna of the Posidonienschiefer is dominated by pelagic organisms. Nektic fauna (free swimming ammonites, fish, ichthyosaurs and plesiosaurs) are the most spectacular and well studied fossils. The normal benthic fauna present in most Liassic soft-bottom communities elsewhere in the Posidonienschiefer (encrusting brachiopods, bivalves, serpulid worms, and crinoids) are not ubiquitously distributed, but are found attached to substrates that must have floated in the pelagic realm before sinking (Seilacher *et al.*, 1985). A thin-shelled benthic marine fauna is restricted to colonies found growing on ammonite shells, driftwood, and in occasional patches on the sediment surface (Kauffman, 1981). Some horizons exist in which articulated bivalves (*Posidonia*) formed a carpet of shells along the bottom. These shells show no evidence of transport and are interpreted to have been indigenous and preserved *in-situ* (Kauffman, 1981). Abundant benthic forams and ostracods also occur in distinct horizons (Riegraf, 1985).

Savrda and Bottjer (1987) ascribed the occurrence of horizons of shelly benthic fossils within laminated, organic-rich strata of the Monterey Formation (Miocene, California) to the development of an "exaerobic zone" at the bottom of a warm, shallow epicontinental seaway. The "exaerobic zone" is defined as "the environment near the dysaerobic/anaerobic boundary (0.1 to 0.2 ml l^{-1} dissolved oxygen) that is characterized by deposition of laminated strata and anomalous

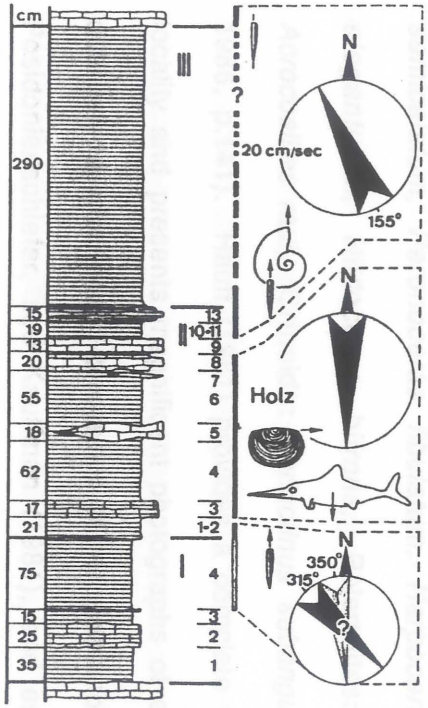


Fig. 1. Bottom current directions (heavy arrows) in the Posidonia Shales (lower Toarcian) of the Holzmaden section. Small arrows indicate the preferred current orientation of measured fossils.

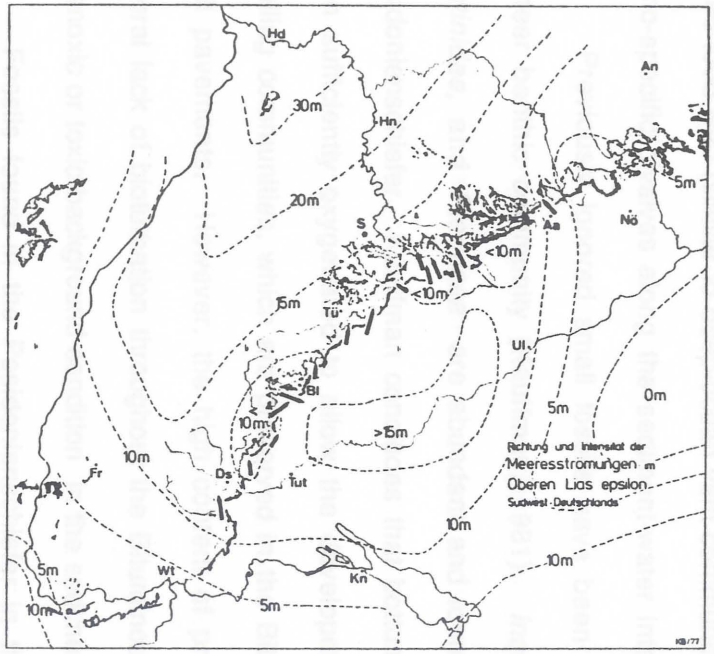


Fig. 2. Paleocurrents in the Upper Posidonia Shales (Upper epsilon = III in Fig. 1) are significantly related to the bottom topography expressed by isopachs. The length of the arrows indicates relative intensity of the currents derived from the degree of the belemnite's current alignment.

Figure 8. In Figure 1, I = Lower Lias epsilon, II = Middle Lias epsilon, III = Upper Lias epsilon. Note the abrupt change in current direction just before the boundary of the Middle and Upper Lias, the location of the two Schlacken beds. (Figures 1 and 2 from Brenner and Seilacher, 1978). Compare Figure 2 with Ziegler's paleogeographical reconstruction (Figure 3) to see that the NNW currents flowed perpendicular to the shore of the Bohemian Massive. This suggests that an offshore wind system may have developed during the transition from Middle to Upper Lias deposition.

occurrences of shelly faunas". They propose that a sulfate-reducing bacteria-based food web (similar to deep-ocean vent communities) could support a bloom of mono-specific bivalves along the sediment-water interface.

Previously ignored small fossils have been identified as members of a pioneer benthic community (Kauffman, 1981). *Inoceramus, Ostrea, Plicatula, Pectinidae,* and *Pteriacea* are abundant and found in patches throughout the Posidonienschiefer. Kauffman concludes that bottom water conditons may have been sufficiently oxygenated to allow the development of low-diversity bottom-dwelling communities, which are preserved in the Bituminous Shale as horizontal shell pavements. However, the high content of preserved organic matter and general lack of bioturbation throughout the Bituminous Shale provide evidence of an anoxic or toxic background condition in the sediment.

Fossils found in the Posidonienschiefer in the Holzmaden area include: Molluscs- *Steinmannia bronni (= Posidonia), Pseudomonotis substriata, Inoceramus dubius,* Ammonites: *Lytoceras siemensi, Dactylioceras commune, D. semicelatum, Peronoceras fibulatum, Harpoceras falcifer, H. elegans, H. elegantulum, Hildoceras bifrons,* Belemnites: *Passaloteuthis paxillosa, Acrocoelites raui,* Crinoids: *Seriocrinus subangularis* (Geyer and Gwinner, 1986, p.141). Hauff (1981) provides a complete faunal list for the Holzmaden locality and presents magnificent photographs of each main faunal group. For detailed description and discussion of the paleontology and paleoecology of the Posidonienschiefer, see Kauffman (1981), and especially Riegraf (1984) and references included therein.

Posidonia, Inoceramus, phosphatic fish remains and belemnite fragments are the most common fossils identified in thin section. The appearance and identification of these fossils in thin section is described in the petrology sections.

Review of Previous Geochemical Research

Kuspert (1982) studied the organic matter of the Posidonienschiefer by petrography, infra-red spectroscopy, column chromatography, and capillary-gas-liquid chromatography. He measured total organic carbon (TOC) by Whole Rock-Eval analysis as ranging from between 2 and 18% throughout the Bituminous Shale facies and 2% in the Schlacken. Moldowan *et al.*, (1985) confirmed anomalously high TOC in the bituminous shales (by LECO analyser) with values ranging from 9 to 14%. Moldowan characterized the organic matter throughout the Posidonienschiefer as marginally mature.

Kuspert reported that the elemental composition of the organic matter from the Bituminous Shale did not differ from that of the Schlacken. Both lithologies showed an H/C ratio = 1.30, O/C ratio = 0.09, and N/C ratio = 0.019. Kuspert and Moldowan both classified the organic matter as Type 2 oil-prone kerogen (after the method of Tissot *et al.*, 1974). The high level of hydrogen saturation and restricted values of ^{13}C suggest that the source of organic matter was largely lipid and fatty-acid rich marine algae. Kuspert concluded that the main source of original organic matter was non-calcareous phytoplankton.

Kuspert (1982) also studied the carbon and oxygen stable isotopes of organic matter and carbonate fractions from several lithologies of the Posidonienschiefer. A comparison of Kuspert's data from the Schlacken versus the

overlying Bituminous Shale reveals interesting variations in the units (Table 1.)

	Bituminous Shale	Schlacken
% carbonate	40.0	75.0
% organic matter	8.0-12.0	2.0
$\delta^{13}C$ carbonate	+ 1.5	- 2.0
$\delta^{13}C$ kerogen	- 27.0	- 28.0

Table 1. Comparison of geochemical data from analysis of the Bituminous Shale and the Schlacken (data from Kuspert, 1982).

Moldowan's (1985) measurements of ^{13}C of the organic matter in the Bituminous Shales, between -27 and -31 $^{o}/oo$, confirm the results of Kuspert (1982). Both Schlacken beds show similar isotope signatures, notably a depleted ^{13}C value. Kuspert interpreted the depleted ^{13}C value to indicate early cementation in the sulfate reduction zone of an anaerobic sediment.

The Dispute About Depositional Environment

Various workers on the paleoecology and sedimentology of the Posidonienschiefer disagree about the exact sedimentary and ecologic conditions during deposition. A detailed study of the petrography, paleontology, and sedimentology of ten outcrops led Einsele and Mosebach (1955) to conclude that the Posidonienshiefer was deposited under gyttja-type conditions, i.e., that

oxygenated and nutrient-rich benthic waters overlaid an anaerobic sediment and that the aerobic/anaerobic boundary was restricted to the sediment-water interface.

Seilacher, Reif, and Westphal (1985, p.5) recognized the Holzmaden locality of the Posidonienschiefer as the representative "Stagnation" Fossil Lagerstätten deposit. They define Fossil Lagerstätten as

> ... rock bodies unusually rich in palaeontological information, either in a quantitative or qualitative sense. This means that the term embraces not only strata with an unusual preservation, but also less spectacular deposits such as shell beds, bone beds and crinoidal limestones... Fossil Lagerstätten are considered as end members of ordinary sedimentary facies, in which the unusual amount and quality of the palaeontological test bodies allows us to identify better the factors responsible for such a facies at all levels of its genesis: biotope conditions (palaeobiology), fate of the soft parts and organic skeletal material (necrolysis), sedimentary transport and burial (biostratinomy) and fate of the mineralized skeletons (fossil diagenesis).

Seilacher has worked on many aspects of the Posidonienschiefer (Seilacher *et al.*, 1976, Brenner and Seilacher 1978, Seilacher 1982a and b, are a few examples). Seilacher interprets the depositional environment as a silled basin with a sapropel rather than a gyttja bottom condition. Evidence that supports Seilacher's conclusion includes the high content of organic matter and pyrite, thin horizontally continuous laminations in the most bituminous shale sections, preservation of articulated skeletons and even certain soft parts, and a fossil fauna consisting mostly of upper-water column organisms. Brenner and Seilacher (1978) summarized their interpretation of the Posidonienschiefer as an ancient analog to that of the modern Black Sea, i.e, a large silled basin with oxygenated pelagic waters overlying a stagnant benthic water-column and anoxic sediment.

Seilacher (1982b) refined this interpretation to account for paleocurrent and paleontological evidence that indicated the stagnation model was inappropriate to explain the entire sequence of the Posidonia shales. Seilacher, Reif, and Westphal (1985) also concluded that there was little sediment influx from the basin margins and that storm-induced water mixing events allowed the short-term establishment of small-sized and monotypic benthic faunas at certain horizons. They maintain that current and oxygenation events are represented in the shale sequence but that the normal depositional background was that of a stagnant basin with sapropelic bottom conditions. Seilacher provides no quantitative estimate of water depth; in fact, he has referred to the Holzmaden locality as representing both shallow and deep water environments in different publications. No structural evidence has yet been reported to substantiate the existence of a sill during Posidonienschiefer deposition (Kauffman, 1981).

Based upon a detailed re-examination of the paleoecology of the Posidonienschiefer, Kauffman (1978, 1981) differed with Seilacher and partially re-affirmed the conclusion of Einsele and Mosebach (1955) that the Posidonienschiefer was deposited under gyttja-type conditions. His case for supporting a modified gyttja interpretation is based upon several lines of evidence. Current-aligned fossils and sedimentary structures suggest water column mixing and the opportunity for oxygenation. Far too many benthic invertebrates are preserved throughout the Posidonienschiefer to be accounted for as "drop fauna" from floating substrates, instead they most likely represent an indigenous benthic fauna. Encrusting epibionts have colonized the upper side of ammonite tests that have settled on the sea floor which provided a substrate elevated above the hostile

sediment. Kauffman has noted epibiont zoning by degree of oxygen tolerence reaching from the sediment surface to what would have been the highest point of elevation above the sediment, thus indicating an anaerobic sediment and gradually increasing oxygenation upwards from the sediment/water interface. This point has been refuted by Seilacher (1982b) and is discussed in more detail later in this thesis.

Kauffman modified the gyttja interpretation by proposing the development of an algal or fungal (but not bacterial) mat at the sediment/water interface as a mechanism for maintaining the aerobic/anaerobic boundary at or very near the sediment/water interface, despite the effects of bottom currents.

Summary

The long-term, background depositional environment of the Posidonienschiefer is yet unresolved. Seilacher and Kauffman disagree about the location of the aerobic/anaerobic boundary in relation to the sea floor. Seilacher argues for a sapropel model, while Kauffman argues for a modified gyttja model (Figure 9). Kauffman has proposed that an algal/fungal mat developed at or near the sediment water interface which sustained anoxic conditions in sediment pore waters. The debate suggests several questions which could be tested by a petrographic study. Remains of an algal mat should be evident as some type of stromatolitic fabric in the Bituminous Shale. A comparative study of the Bituminous Shale and the Schlacken should reveal paleontological, sedimentological, and diagenetic evidence that will help resolve the debate about depositional environment.

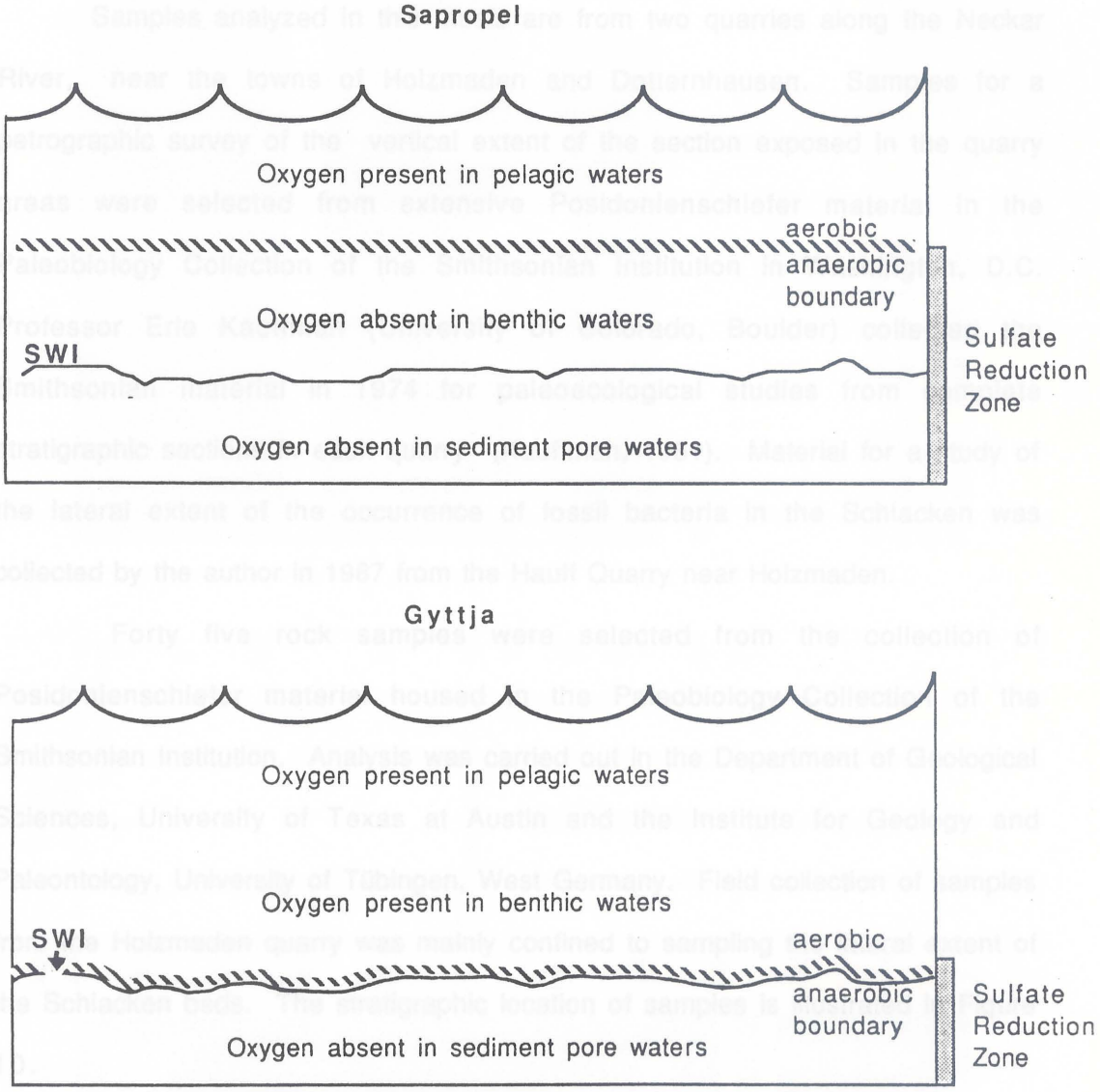


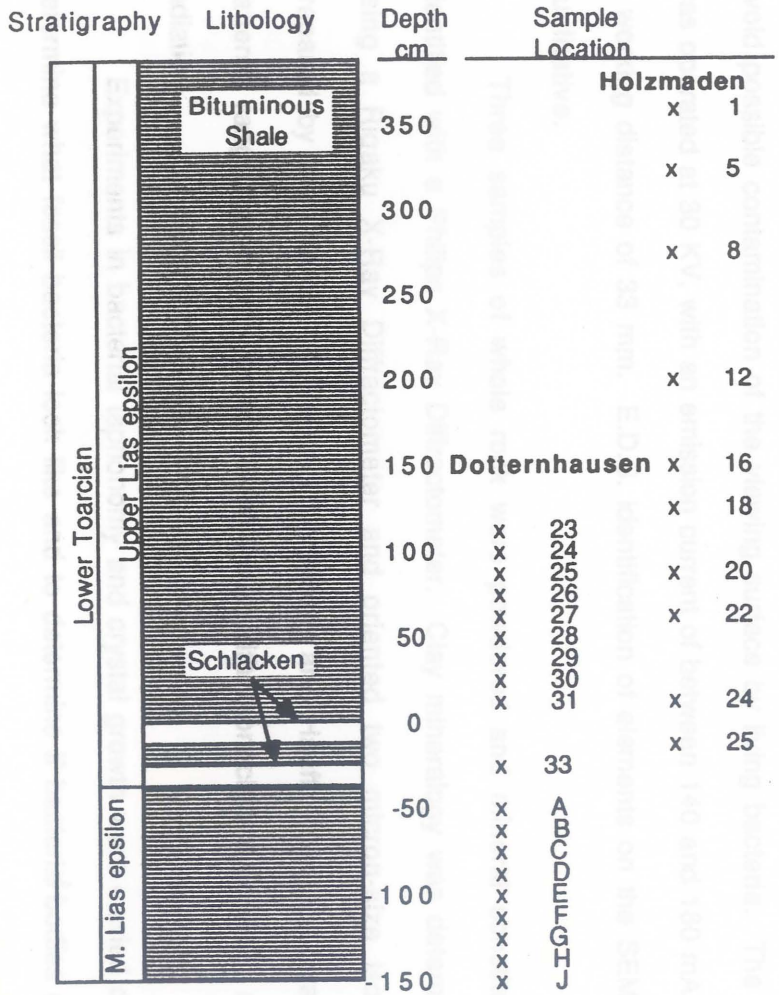
Figure 9. Comparison of Seilacher's depositional environment model (top) with Kauffman's (bottom). The main point of disagreement is where in the water column to locate the aerobic/anaerobic boundary.

Methods

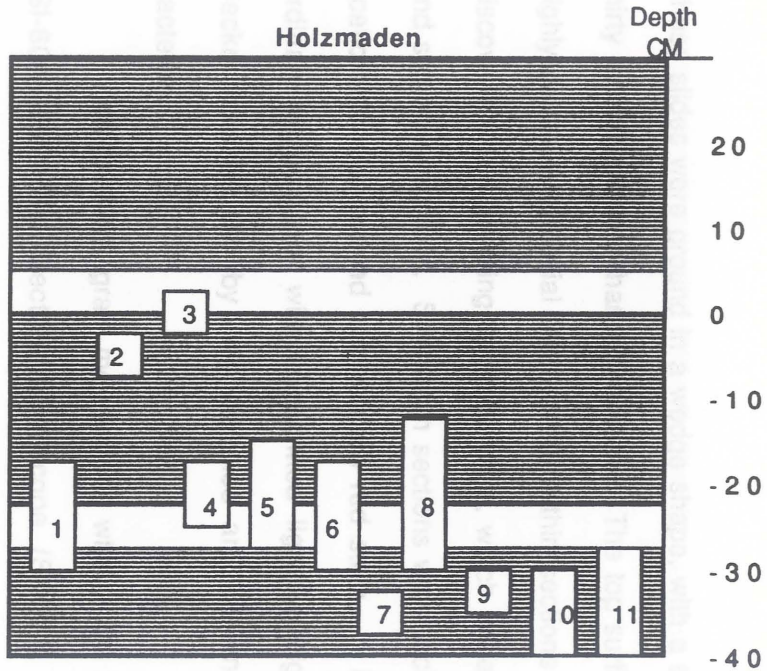
Samples analyzed in this thesis are from two quarries along the Neckar River, near the towns of Holzmaden and Dotternhausen. Samples for a petrographic survey of the vertical extent of the section exposed in the quarry areas were selected from extensive Posidonienschiefer material in the Paleobiology Collection of the Smithsonian Institution in Washington, D.C. Professor Erle Kauffman (University of Colorado, Boulder) collected the Smithsonian material in 1974 for paleoecological studies from complete stratigraphic sections in each quarry (Kauffman, 1981). Material for a study of the lateral extent of the occurrence of fossil bacteria in the Schlacken was collected by the author in 1987 from the Hauff Quarry near Holzmaden.

Forty five rock samples were selected from the collection of Posidonienschiefer material housed in the Paleobiology Collection of the Smithsonian Institution. Analysis was carried out in the Department of Geological Sciences, University of Texas at Austin and the Institute for Geology and Paleontology, University of Tübingen, West Germany. Field collection of samples from the Holzmaden quarry was mainly confined to sampling the lateral extent of the Schlacken beds. The stratigraphic location of samples is illustrated in Figure 10.

Fifty thin sections were prepared from two major lithologies, the Bituminous Shale and the Schlacken. Sections were impregnated with blue epoxy and ground without water to prevent clays from swelling. Several experimental slides were prepared especially to help in locating and studying fossil bacteria.



A.



B.

Figure 10. Stratigraphic location of samples. A) Samples selected from Smithsonian collection. B) Samples collected from the Hauff Quarry, Holzmaden. Note scale change between A and B.

These slides were ground in a wedge shape, with a tapered thickness ranging from thirty microns to less than ten microns. The top surfaces of the thin sections were highly polished. Special preparation of thin sections turned out to be essential for discovering and studying fossil bacteria, which appear as one to two micron rods and spheres in calcite. Some thin sections were etched with dilute hydrochloric or acetic acid and stained with alizarin red stain. A light-diffusion technique using ordinary white paper with transmitted light (Delgado, 1977) helped filter out Becke lines caused by clay particles and illuminated otherwise cryptic fossil bacteria.

Thin sections, grain mounts, and whole rock samples were studied with an ISI-60A Scanning Electron Microscope (SEM). SEM samples were freshly fractured, ground or etched, and immediatly coated with carbon and/or gold to avoid possible contamination of the viewing surface by living bacteria. The SEM was operated at 30 KV, with an emission current of between 140 and 180 mA, and a working distance of 33 mm. E.D.S. identification of elements on the SEM was qualitative.

Three samples of whole rock were powdered and mineral constituents identified with a Philips X-Ray Diffractometer. Clay mineralogy was determined using a Rigaku X-Ray Diffractometer and oriented two micron-size isolates prepared by the method of Starkey, Blackman, and Hauff (1984). Diffraction patterns ranged from 2° to 28° Two Theta with monochromatic Cu-K alpha radiation.

Experiments in bacterial taphonomy and crystal growth were carried out to determine what fossil bacteria look like and to determine if bacterial bodies could

be trapped inside growing mineral crystals. Details of the procedure are included in the Experiments with Bacteria section.

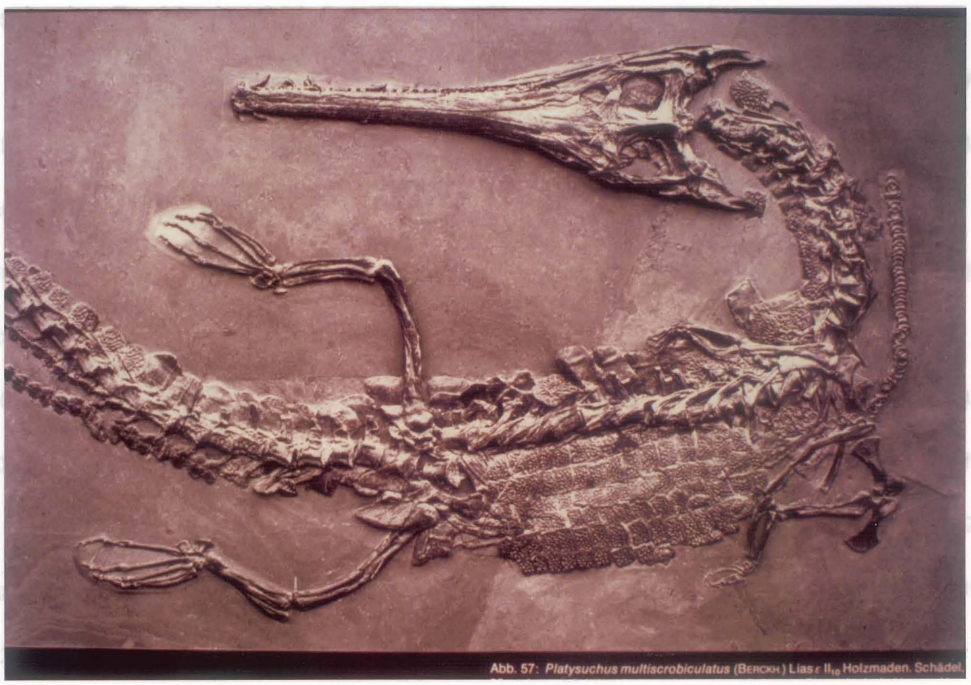
Petrology of the Bituminous Shale

Three paleoecological observations based upon previous studies of the Bituminous Shale suggest that at the sediment/water interface and downward, pore-waters of the organic-rich clay sediment were dysaerobic to anaerobic.

Paleoecological studies of the Posidonienschiefer by Kauffman (1981), Seilacher (1976, 1982, 1985) and Riegraf (1984), indicate that the benthic community was severely impoverished. The low quantity, low diversity, and small size of benthic fossils and lack of bioturbation indicates that the sediment was hostile to bottom dwellers, particularly infaunal benthos.

Superbly preserved vertebrate fossils found in the Bituminous Shale are almost always prepared from the bottom side, not the top (Figure 11). The fossil carcasses of large marine reptiles consistently exhibit better preservation on the down-facing side and often show signs of bacterial decay and even macro-faunal scavenging on the top side (Kauffman, 1981). The bottom surface of the carcass would have been imbedded in the soft sediment as it lay on the bottom after death. This suggests that aerobic degraders were active in the water column near the sediment surface but less active in the sediment.

In certain horizons within the Bituminous Shale, ammonite shells may have acted as "Benthic Islands" for encrusting epibionts that needed oxygen (Kauffman, 1981). Kauffman reported that ammonite fossils are encrusted only on the top side, and that the encrusting biota is "zoned" according to inferred oxygen tolerance levels. The epibionts were benthic types such as the oyster *Ostrea* , serpulid worms, the inarticulate brachipod *Orbiculoidea,* and other



97 cm

Figure 11. This *Platysuchus*, a marine crocodile, has been prepared from the bottom side. The detailed state of preservation , including bits of preserved skin or plates along the bottom edge, is common in Posidonien schiefer vertebrates. In the rare case in which the top side of a fossil is prepared, the remains are scattered and decayed as though aerobic macro- and micro-degraders had scavenged the carcass from the top down. (Photo from Hauff, 1981, See Kauffman, 1981, figs.12-18 for more detailed illustrations.)

byssal bivalves. These encrusters are the type expected to flourish on the sediment surface but instead are found to be restricted to the upper surfaces of fossils in the Posidonienschiefer (Figure 12).

Seilacher (1982) re-studied ammonite encrustation and disagreed with Kauffman's interpretation. Seilacher counted and measured the orientation of encrusting organisms on both sides of 25 large ammonite shells from the Bituminous Shale and found that encrusters were nearly equally distributed and had colonized the shells while the ammonite lived in the upper water column. My own observations indicate that even small ammonites are encrusted with large epibionts (Figure 13). It seems unlikely that a free-swimming pelagic ammonite could exist with such large attached encrusters. The epibionts must have colonized at least some ammonites once the shell reached the sea floor. Perhaps these shells provided enough elevation above a zone of toxic conditions at or slightly above the sediment/water interface to allow opportunistic benthic organisms to survive. Shells encrusted on both sides may also have been flipped over at some point in their depositional history.

The Bituminous Shale is a Fossiliferous Laminated Illite Claystone (Folk, 1974). The color of the dry rock is Medium Gray (N5). Unweathered rock is laminated but not fissile. No structural deformation is evident besides compaction. The Bituminous Shale contains small (1-15 mm) calcite fossils, phosphatic belemnite and fish debris (< 1 mm to 10 mm). Rare articulated *Inoceramus* and *Posidonia* shells and most other allochems lie parallel to bedding. Calcite prisms

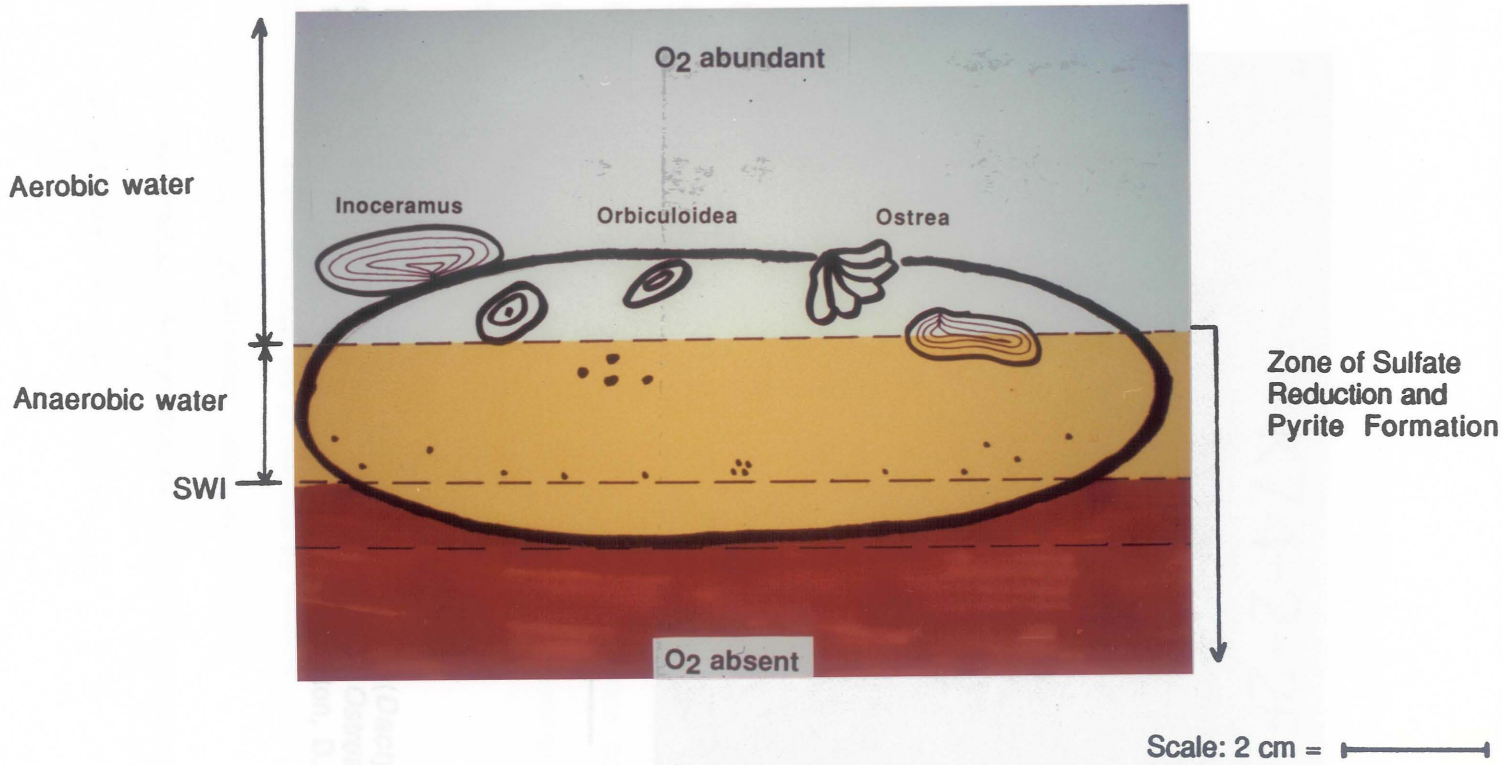


Figure 12. Schematic diagram of how an ammonite shell (the large dark elipse in the above figure) which settled on a muddy ocean floor could act as a point of elevation above a toxic substrate and provide attachment sites for aerobic epibiont encrusters.

Figure 13. Top-side view of a small ammonite (*Dactylioceras*) encrusted by comparatively large epibionts, chiefly the oyster *Ostrea*. The speciman is from the collection of the Smithsonian Institute, Washington, D.C.

from disarticulated *Inoceramus* and *Posidonia* occur commonly as individual grains.

Twenty thin sections of the Bituminous Shale from both Holzmaden and Dotternhausen quarries were studied. Thin sections were impregnated with blue epoxy under pressure. No blue areas were observed except where recent cracks had developed during thin section preparation. Porosity has been primarily occluded by clay compaction.

The Bituminous Shale is composed of a carbonate-rich clay matrix, organic matter, pyrite, calcite and phosphatic fossils, spores, quartz silt, and little carbonate cement. A point count (200 points) of sample K74-2-25 which is representative of the homogeneous Bituminous Shale is reported in Table 2.

The Bituminous Shale is composed of the same constituents as the Schlacken but in different proportions. Most notably the clay content is higher than in the Schlacken, concentration of macro-fossils is lower, and the cement content is very low. The matrix was considered as a Terrigenous component in calculating Fundamental End Member categories. This sample belongs to the Terrigenous class of sedimentary rock (Folk, 1974).

Mineral Composition. Descriptions of each of the main constituents of the Bituminous Shale lithology are presented as follows:

1. Terrigenous Minerals : clays and quartz.
2. Allochems: macrofossils, microfossils, spores, organic matter.
3. Orthochems: calcite, pyrite.

Constituent	Points	Percent
Clay Matrix	113	56.5
Quartz Silt	6	3.0
Mica flakes	0	0.0
Macrofossils	13	6.5
Spores	2	1.0
Organic matter	42	21.0
Spar	1	0.5
Framboidal Pyrite	15	7.5
Massive Pyrite	2	1.0
Plucked Grains/Unknown	6	3.0
Total	**200**	**100**

Fundamental End Members

Terrigenous	Allochemical	Orthochemical
59.5%	28.5%	9.0%
Error ±3.2%	±3.1%	±2.2%

Table 2. Constituents and percent composition (by area) of a representative sample of the Bituminous Shale (Sample K74-2-25, Dotternhausen).

Clays

X-Ray Analysis. Eight samples of clay-fractions for X-Ray analysis were prepared using the procedure of Starkey, Blackman, and Hauff (1984), modified at several steps. Samples were crushed, soaked in distilled water, sieved to remove the less than 75μm size fraction, deflocculated, ultrasonically disaggregated, and allowed to settle. The <2μm size fraction was pipetted onto glass slides (in triplicate) and air dried. Several control samples were millipore-filtered instead of pipetted and air dried. The millipore filter technique resulted in superior clay orientation and X-Ray results. One of each triplicate samples was treated with ethylene glycol to expand swelling clays. The third of the triplicate samples was heat treated to collapse expansive and unstable clays. All three samples were X-rayed together from 2-28° Two-Theta.

The clay minerals of the Bituminous Shale listed in order of relative abundance are as follows: illite, illite-smectite mixed layer clays, minor kaolinite, chlorite, quartz, and calcite (Figure14). Illite was identified by a peak at 10Å that persisted through glycolation. Illite/smectite mixed layer clay was identified by the broad range of small peaks and asymmetries on the low side of the 10Å illite peak. Glycolation exaggerated the illite peak asymmetry. A minor amount of chlorite was identified by peaks at 14, 7, and 3.5Å. Kaolinite was not definitively confirmed, but persistent peaks at 7Å and on the low side of 25Å suggest that a minor amount of kaolinite is present.

The most obvious and interesting result of the clay fraction X-Ray analysis is that both the mineralogy and the proportional abundance of various clays in each

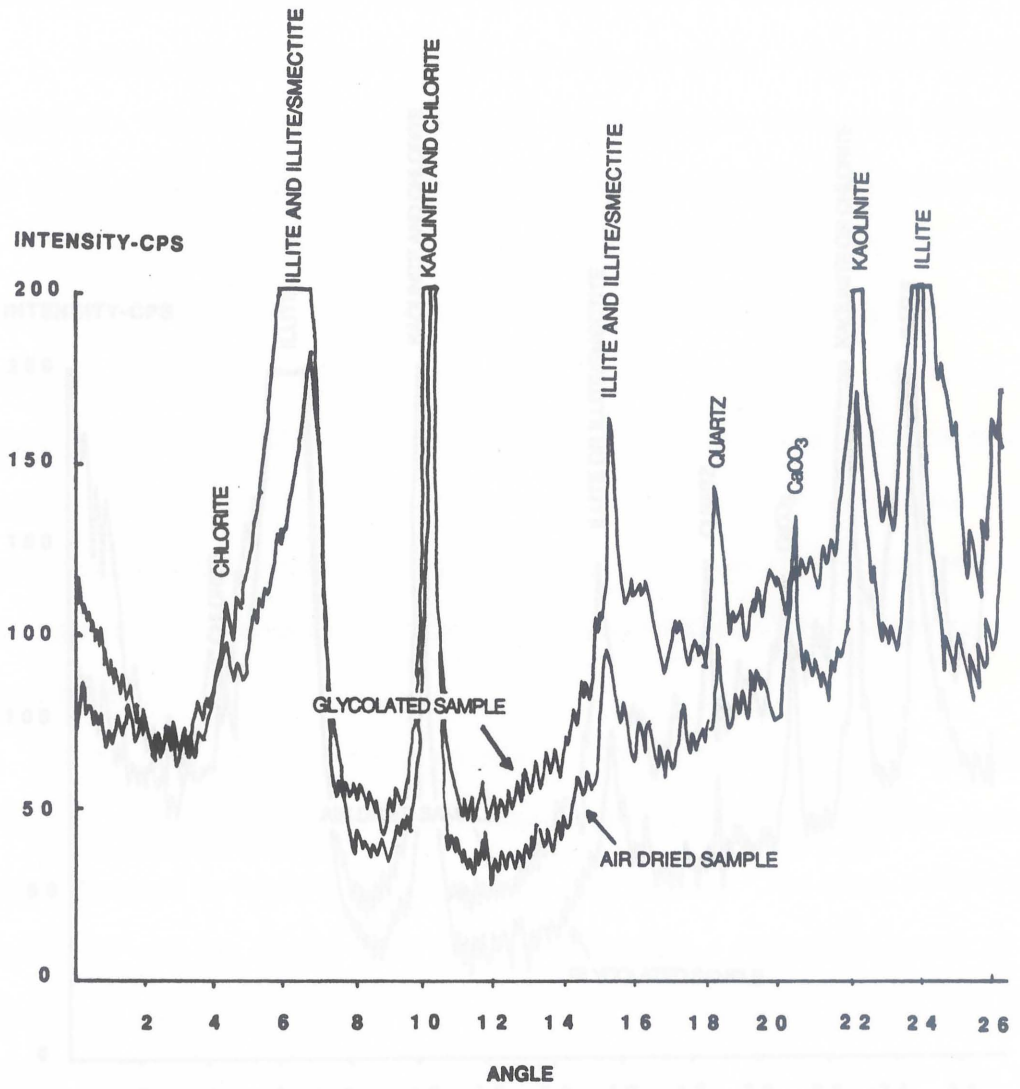


Figure 14. X-ray analysis of the < 2μ clay fraction of the Bituminous Shale. Results from an air-dried and glycolated sample are presented together.

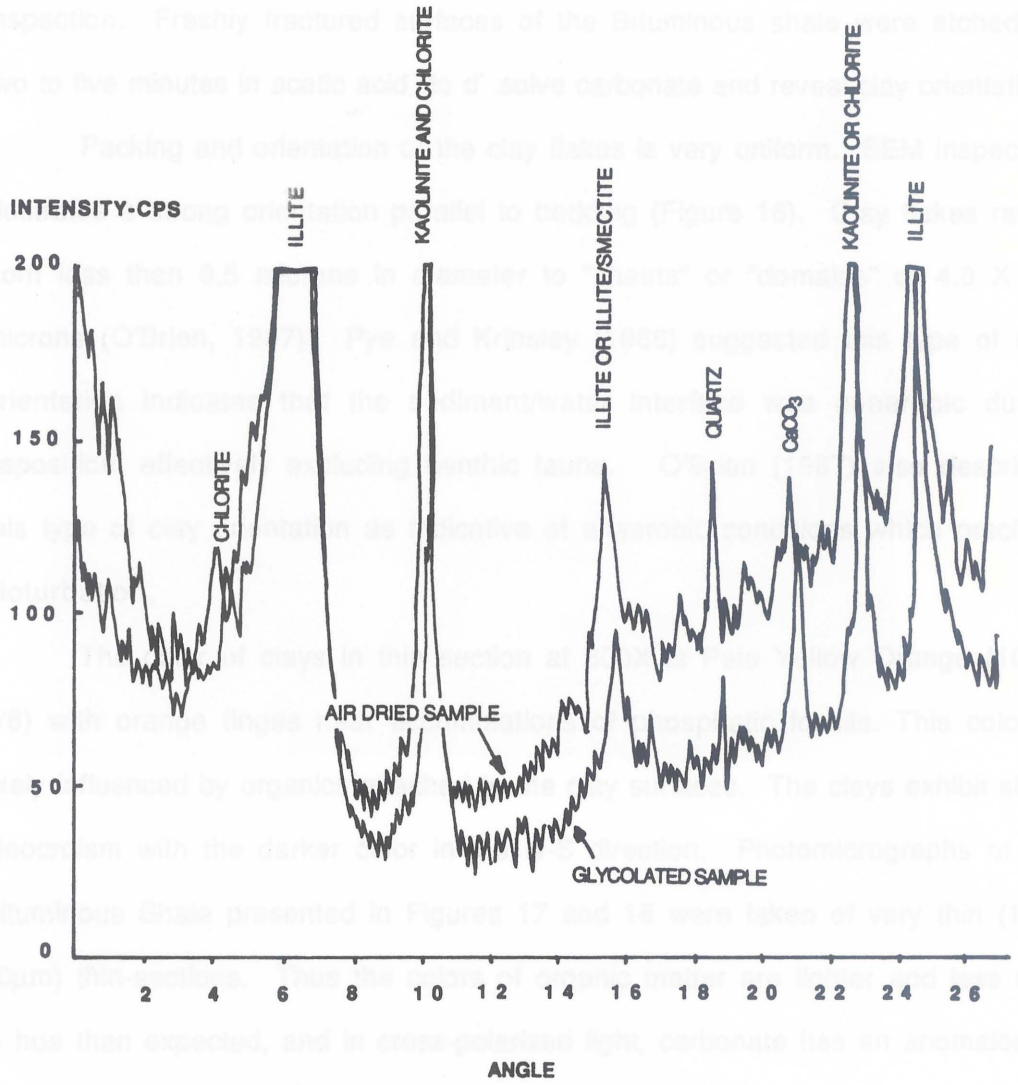


Figure 15. X-ray analysis of the < 2μ clay fraction of the Schlacken. Results from an air-dried and glycolated sample are presented together.

lithology are very similar (compare Figure 14 and 15). This suggests that the source of clays was the same throughout the deposition of both lithologies.

Fabric Analysis. Shale fabric and clay orientation was studied by SEM inspection. Freshly fractured surfaces of the Bituminous shale were etched for two to five minutes in acetic acid to dissolve carbonate and reveal clay orientation.

Packing and orientation of the clay flakes is very uniform. SEM inspection illustrates a strong orientation parallel to bedding (Figure 16). Clay flakes range from less than 0.5 microns in diameter to "sheets" or "domains" of 4.0 X 8.0 microns (O'Brien, 1987). Pye and Krinsley (1986) suggested this type of clay orientation indicates that the sediment/water interface was anaerobic during deposition, effectively excluding benthic fauna. O'Brien (1987) also described this type of clay orientation as indicative of anaerobic conditions which preclude bioturbation.

The color of clays in thin section at 600X is Pale Yellow Orange (10YR 8/6) with orange tinges near accumulations of phosphatic fossils. This color is likely influenced by organics attached to the clay surfaces. The clays exhibit slight pleocroism with the darker color in the N-S direction. Photomicrographs of the Bituminous Shale presented in Figures 17 and 18 were taken of very thin (10 - 20μm) thin-sections. Thus the colors of organic matter are lighter and less rich in hue than expected, and in cross-polarized light, carbonate has an anomalously vivid birefringence (Figure 17-B).

Figure 16. Magnification = 1,500 X, scale bar = five microns. Acetic acid etched Bituminous Shale surface. Acid has dissolved away carbonate thus accentuating clay fabric. Note clay orientation parallel to bedding.

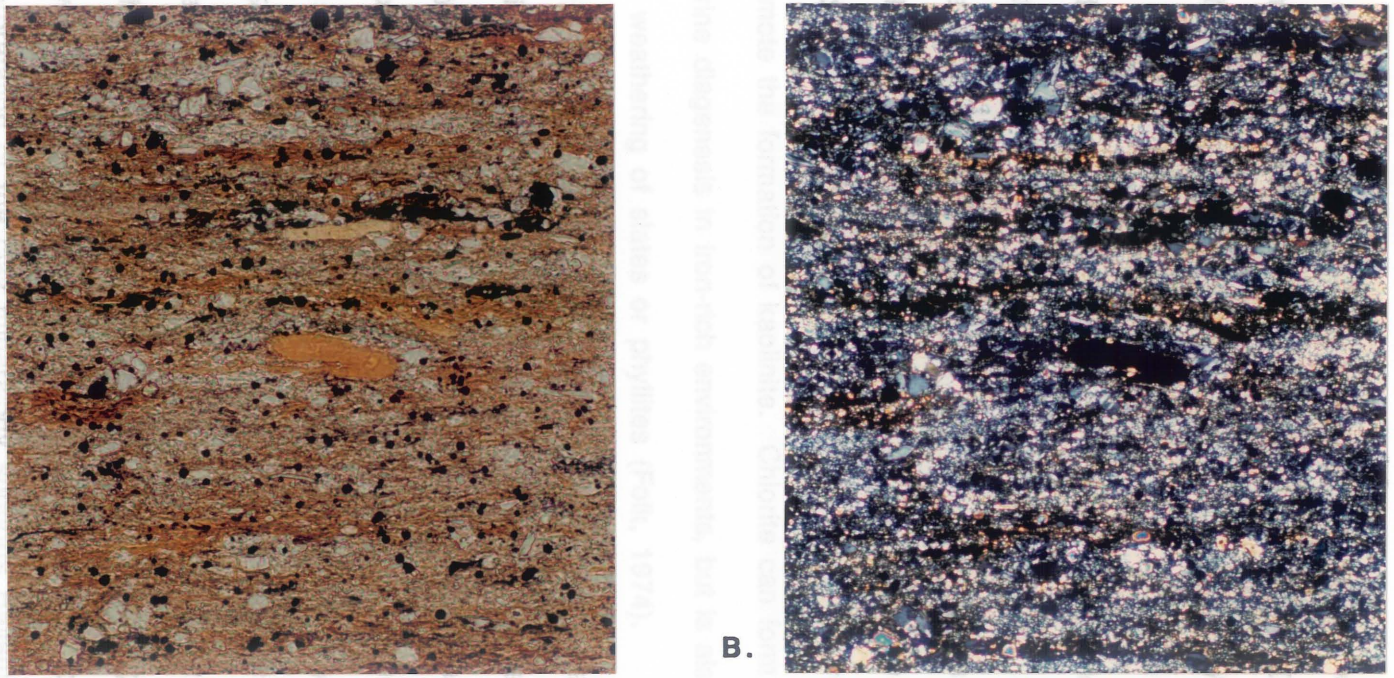


Figure 17. Magnification = 200 X. Representative view of the Bituminous Shale illustrating several common features. In Figure A, photographed with normal transmitted light, note: 1) ubiquitous reddish-brown amorphous organic matter in wisps parallel to bedding, 2) bright yellow collapsed *Tasmanites* spore 3) homogeneously disseminated framboidal pyrite, 4) scattered quartz silt, 5) phosphatic fossil oriented parallel to bedding, 6) carbonate grains showing evidence of partial dissolution. Figure B, photographed in crossed polarized light, note: vivid birefingence of carbonate grains due to unusually thin thin-section (15 - 20 microns thick). Phosphatic fossils, pyrite and areas of thick organic matter appear black.

Clays are predominantly of detrital, not diagenetic, origin. Although a minor amount of kaolinite is indicated by X-Ray Diffraction, no evidence of authigenic clays was observed in thin section or by SEM inspection.

Potassium and iron-rich illite forms from the weathering of "acid" rocks and during soil formation in temperate to semi-arid climates. Illite/smectite mixed-layer clays form when potassium ions are stripped from illite during weathering. Degraded illite may regain some potassium ions as it enters the sea and revert to illite. Intense chemical rock-weathering in equatorial to sub-tropical climates can completely leach potassium from clay-forming soils and promote the formation of kaolinite. Chlorite can form diagenetically during early marine diagenesis in iron-rich environments, but is also common as the result of the weathering of slates or phyllites (Folk, 1974).

The Posidonienschiefer in southern Germany has not been altered by deep burial or metamorphism (Moldowan *et al.*,1985); therefore, the clay mineralogy may be assumed to represent original depositional constituents. The location of depositional environment in relation to the source shoreline may be inferred by the relative abundance of illite, illite/smectite, and kaolinite in a shale (Weaver, 1958). Kaolinite is most abundant nearshore, illite most abundant offshore and illite/smectite most abundant in between. The low kaolinite/illite ratio in the both the Bituminous Shale and the Schlacken suggests that the depositional environment was far removed from the fluvial source of sediment. This interpretation of the clay mineralogy supports Hallam's (1981) general scenario

for the Toarcian of central Europe as a low-energy seaway receiving sediment from a low-relief, humid, tropical, soil-producing terrain.

Quartz

Common quartz grains ranging from silt-size (4 to 65μm diameter) to fine sand-size (up to 250μm diameter) are common but not volumetrically important in the Bituminous Shale (Figure 17). Most grains show straight to slightly undulose extinction. Fine-sand sized grains may contain bubble trains of fluid inclusions. Quartz silt and fine sand is randomly mixed with fossil fragments, organic matter and clays. The sand grains are subequant and well rounded. Grains are too small to show definitive evidence of etching or surface dissolution features. No grains have diagenetic overgrowths.

Allochems

Fossils. The Bituminous Shale consists of approximately 6.5 percent fossils and fossil fragments. Phosphatic fossils include belemnite hooks, fish-bone fragments, and inarticulate brachiopod shells. Calcite *Inoceramus* and *Posidonia* shells occur mainly as disarticulated prisms (Figure 18). Ammonites are commonly preserved as flat films of periostracum.

Phosphatic fossils range in size from 0.1 to 0.5 mm long. Fragments range from several microns to 0.1mm. The larger phosphatic fossils and fragments are oriented parallel to bedding.

Coccoliths represent a small proportion of the total carbonate fraction in Bituminous Shale as in the Schlacken. The sizes of coccoliths and coccolith

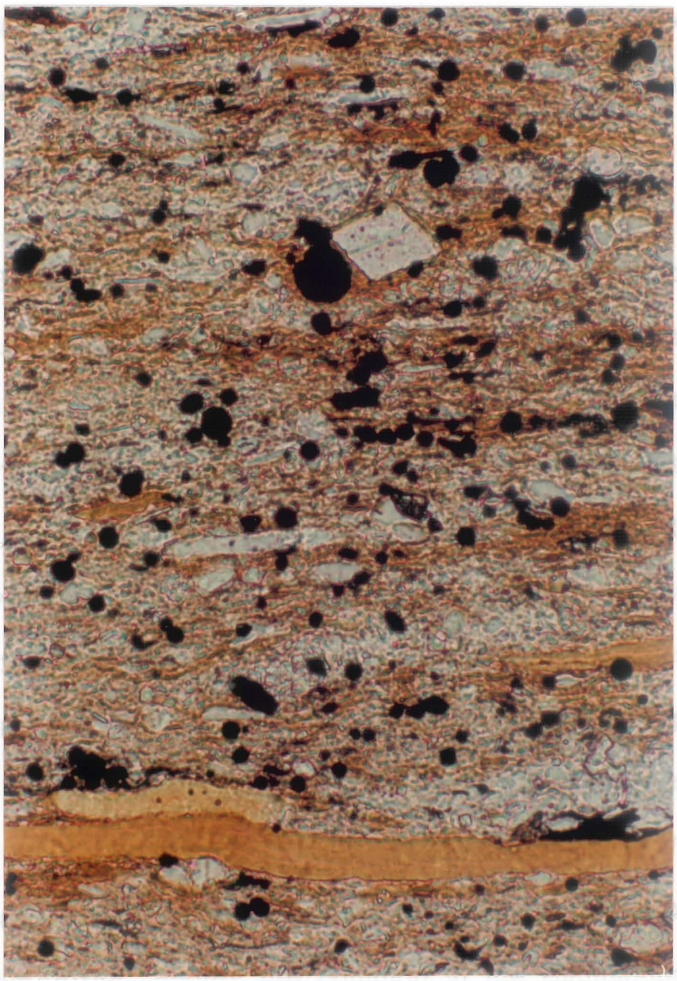


Figure 18. Magnification = 400X. Bituminous Shale. Note the prismatic calcite fragment of a disarticulated *Inoceramus* shell, collapsed *Tasmanites* spore, abundant framboidal pyrite, and phosphatic fossil fragment oriented parallel to bedding.

fragments range from < 0.5μm-12.0μm in diameter. Because of their small size and mixing with clay and amorphous organic matter, coccoliths are apparent as distinct fossils only in the SEM and at the thinnest edge of thin sections.

What first appeared to be large coccolithophores throughout the Bituminous Shale and Schlacken were identified by SEM inspection as the calcareous nannoplankton *Schizosphaerella punctulata* (C. Hemleben, pers. comm., 1987). *S. punctulata* lived from the latest Triassic to the end of the Jurassic, but was most common in the early Jurassic (Perch-Nielsen, 1985). In thin section, they appear as 12-30μm diameter globular calcareous tests with no obvious ornamentation and are easily confused with rounded shell fragments, coccoliths, or areas of clay-rich microspar. The ultrastructure of the test, as revealed by SEM studies, is made of intricately linked 1μm diameter slotted plates and 1μm long rods which form a network of sub-cubic boxes (Kälin, 1980). In Jurassic carbonates of Italy (Ammonitico Rosso and Valmaggiore formation) *S. punctulata* and the fibrous calcite cements which nucleate on their tests form up to 15% of the total rock volume (Kälin, 1980). *S. punctulata* contributes approximately half of the total 6.5% fossil content of the Bituminous Shale.

Tasmanites spores are common in the Bituminous Shale. With few exceptions the spores are preserved in a compressed morphology, parallel to bedding with no internal cement (Figures 17 and 18). These spores were deposited and compressed before diagenetic cements could form in the internal void space and preserve their original spherical shape.

Amorphous organic matter is ubiquitous. Bitumen and kerogen occur mixed with clay in wisps oriented parallel to bedding (Figures 17 and 18). Point counting organic matter resulted in a figure of 21% (by area). Kuspert (1982) reported that TOC ranged from 8-12% (by weight), and analyzed the amorphous organic matter as 10% bitumen and 90% insoluble Type II kerogen.

Orthochems

The very low percentage of orthochemical calcite in the Bituminous Shale is one of the most striking differences between this lithology and the Schlacken. Compaction of inter-granular pore space must have occurred before substantial amounts of diagenetic cement could form. Alternatively, and/or in addition, formation of cements may have been inhibited by a chemical limiting factor.

Rare patches of lenticular microspar are the only examples of orthochemical calcite. This occurrence is most clearly evident in thin- sections cut parallel to bedding (Figure 19).

Pyrite is the only volumetrically significant authigenic mineral preserved in the Bituminous Shale and is the best guide to interpreting its diagenetic history. Pyrite occurs in a variety of morphologies in the Bituminous Shale. Rare but spectacular fossils of *Posidonia* complete with shell ornamentation are replaced by pyrite. Massive blebs of pyrite also occur in shapes that are unrecognizable as having had any biologic precursor. The pyrite blebs cross bedding planes but do not seem to have disturbed bedding or sedimentation.

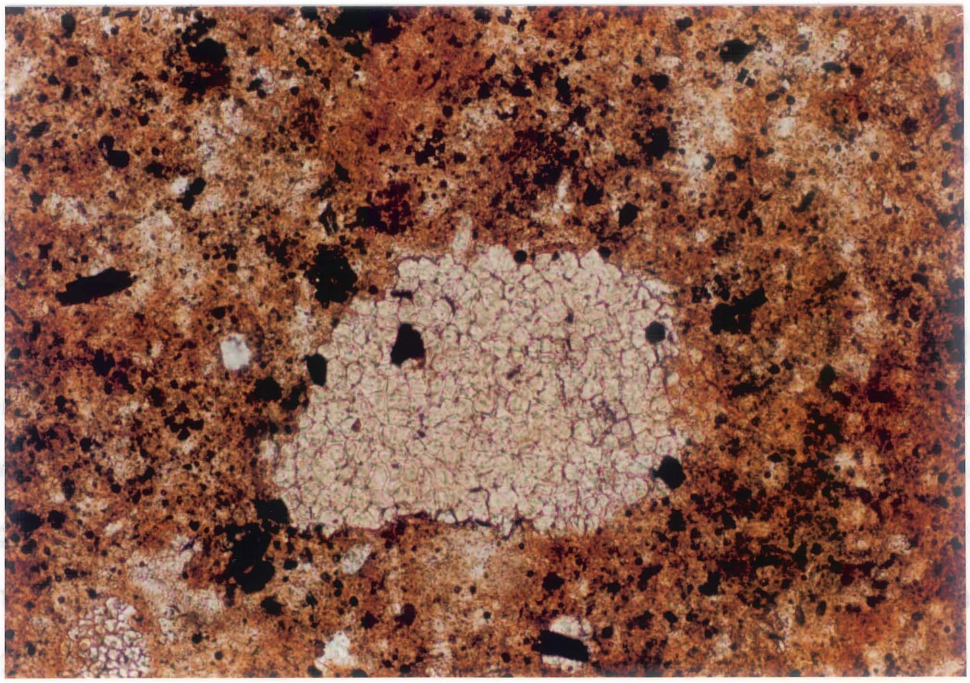


Figure 19. Magnification = 200X. Bituminous Shale, thin section cut parallel to bedding. Rare occurrence of microspar in the Bituminous Shale lithology. Sample k74-16-1, Hauff Quarry, Holzmaden.

Mollusc shells occasionally show partial replacement of individual calcite prisms by massive pyrite. Curiously the calcite prisms adjoining the pyrite replacements are pristine and appear to have no effects of replacement reactions.

Isolated 50μm to 1mm euhedral pyrite rhombs are common. No aggregations occur along bedding planes or around fossil debris.

Framboidal pyrite occurs as isolated spheres and aggregates throughout the matrix shale. Aggregates of framboids are common inside holes within fossils. Individual framboid sizes range from 2-50μm with 10-20μm size the most common. All framboids show very sharp crystal edges and no signs of transport abrasion.

The formation of pyrite (FeS_2) during deposition and early diagenesis is controlled by the availability and state of three com-ponents: reactive detrital iron minerals, dissolved sulfate, and biologically decomposable (= reactive) organic matter (Berner, 1972). Any one of these three compoments can be the limiting factor controlling total pyrite formation. However, in an anaerobic organic-rich marine mud environment, the availability of iron is the most common limiting factor (Berner, 1984).

Many workers have studied processes and products of diagenetic reactions in the sulfate reducing zone of organic-rich muds (see Berner, 1972, and 1984 for comprehensive reviews and bibliographies). The diagram in Figure 20 schematically illustrates the overall process of pyrite formation in an anaerobic, organic-rich sediment.

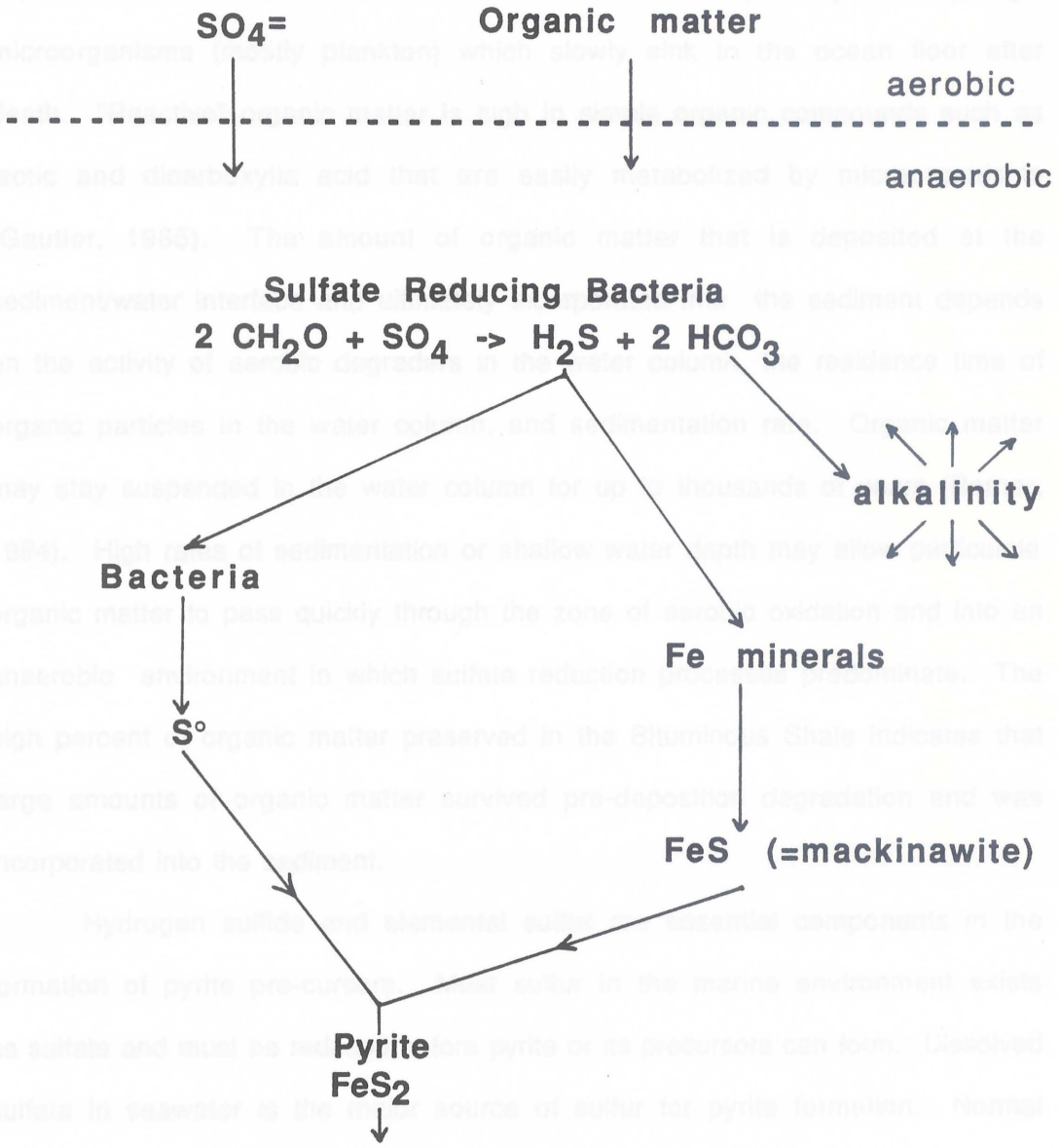


Figure 20. Formation of pyrite in an anaerobic, organic-rich sediment. This process is discussed in the text. Figure adapted from Berner (1971).

The major source of particulate organic matter which is incorporated into the sediment and fuels microbial sulfate reduction is photosynthetic pelagic microorganisms (mostly plankton) which slowly sink to the ocean floor after death. "Reactive" organic matter is high in simple organic compounds such as lactic and dicarboxylic acid that are easily metabolized by microorganisms (Gautier, 1985). The amount of organic matter that is deposited at the sediment/water interface and ultimately incorporated into the sediment depends on the activity of aerobic degraders in the water column, the residence time of organic particles in the water column, and sedimentation rate. Organic matter may stay suspended in the water column for up to thousands of years (Berner, 1984). High rates of sedimentation or shallow water depth may allow particulate organic matter to pass quickly through the zone of aerobic oxidation and into an anaerobic environment in which sulfate reduction processes predominate. The high percent of organic matter preserved in the Bituminous Shale indicates that large amounts of organic matter survived pre-deposition degradation and was incorporated into the sediment.

Hydrogen sulfide and elemental sulfur are essential components in the formation of pyrite pre-cursors. Most sulfur in the marine environment exists as sulfate and must be reduced before pyrite or its precursors can form. Dissolved sulfate in seawater is the major source of sulfur for pyrite formation. Normal seawater contains ample sulfate for pyrite formation; typical values for various oceans range from 2.68 to 2.75 g/kg sulfate in 35% salinity water (Riley and Skirrow, 1965, p.146). Only two pathways are available for the production of

H_2S: 1) bacterial reduction of seawater sulfate to H_2S or, 2) bacterial decomposition of organic compounds with sulfur components (such as proteins and amino acids) to H_2S (Berner, 1984).

In the pore waters of anaerobic muds, sulfate reducing bacteria utilize aqueous sulfate as an electron acceptor to oxidize reactive organic matter to bicarbonate and reduce sulfate to sulfide. Sulfate reducing bacteria are heterotrophs, ie., they utilize existing organic carbon molecules as a source of energy. In addition to sulfur compounds, the microbial degradation of proteins results in the formation of ammonia.

Westrich and Berner (1984) have proved the general stoichiometry of the bacterial sulfate reduction reaction and summarized it as follows:

$$2CH_2O + SO_4^{=} \rightarrow H_2S + 2HCO_3^{-}$$

H_2S is thus available to react with ferous iron to form mackinawite and griegite. The production of bicarbonate increases pore water alkalinity and provides a carbonate source for the precipitation of $CaCO_3$. This reaction can take place in the sediment or in the water column (Gautier, 1985). H_2S may be further oxidized to form elemental sulfur by the sulfur bacteria *Beggiatoacea*, which lives at the aerobic/anaerobic boundary in sediments (R. Aller, pers. comm.). Tappan (1980, p. 22.) reported the reaction as:

$$H_2S + {}^1/_2\, O_2 \rightarrow S^{\circ} + H_2O$$

Elemental sulfur is essential to the formation of the meta-stable pyrite precursors mackinawite and griegite.

Sulfate from seawater is introduced into the sediment by diffusion or by biological mixing (Goldhaber and Kaplan, 1980). The amount and reactivity of the available organic matter (Berner, 1984) and the rate of sulfate deposition and diffusion into the sediment controls the rate of bacterial reduction of sulfate. As clay sediment compacts, the rate of sulfate diffusion through pore waters and the availability of microbial metabolites are restricted, thus slowing pyrite formation.

The availability of iron minerals also may limit pyrite formation. Ferrous iron available for pyrite formation has several possible sources including hematite, limonite, goethite, chlorite, and other iron-oxides and silicates (Berner, 1971). Chlorite is the most important iron-bearing depositional constituent in the Bituminous Shale, but is not abundant. Raiswell and Berner (1985) analyzed the amounts of iron, organic matter, and pyrite sulfur in several samples of the Bituminous Shale and determined that pyrite formation was ultimately limited by the availability of iron.

Raiswell (1982) determined that the morphology of pyrite crystals provides evidence of geochemical conditions in the sediment during deposition and early diagenesis. He studied the relationship of pyrite textures, isotopic composition, and reactive iron content in carbonate concretions from the Liassic Jet Rock Shales of Yorkshire, England (lateral equivalent of the

Posidonienschiefer) and determined the geochemical parameters necessary to form framboidal versus euhedral pyrite. Framboidal pyrite forms when iron monosulfides (mackinawite, greigite) react with elemental sulfur (Berner, 1969a). The reaction must take place in a sediment/pore water system that is anaerobic, yet open enough to allow rapid diffusion of sulfate into the sediment and escape of bicarbonate alkalinity produced as a result of sulfate reduction. Reactive organic carbon must be available to fuel microbial sulfate reduction.

Euhedral pyrite forms in an anaerobic sediment/pore water system in which sulfate diffusion and the transport of other chemical components is restricted. Typically, euhedral pyrite forms in sediments below the zone of framboidal pyrite formation. The concentration of sulfate is diminished because of intense microbial sulfate reduction in the overlying sediment. Sulfate replenishment from sea water is restricted as pore spaces in the muddy sediment are compacted. Compaction also restricts the transport of ferrous iron. The freshly deposited, highly reactive organic matter which fueled rapid sulfate reduction in the upper layers of sediment during framboid production becomes exhausted with depth and leaves lesser amounts of non-reactive organic matter for microbial sulfate reduction in deeper sediments. The reduced availability of reactive organic matter, reactive iron, and slower sulfate reduction rates results in generally slower crystal growth and the formation of euhedral pyrite texture (Berner, 1978). Raiswell (1982) maintains, however, that a slower rate of sulfate reduction is less of a control on pyrite texture than the degree of reactivity

and total amount of organic matter available in the sediment for microbial degradation.

Summary of Depositional Environment

The Bituminous Shale was deposited in a low-energy seaway well off the shore of a tropical, soil-producing source terrain located to the north and east. The upper water-column supported a diverse normal marine fauna. Abundant calcareous nannoplankton produced a large proportion of the carbonate and organic matter preserved in muds at the ocean floor. Pore waters of the ocean-floor mud were dysaerobic to anaerobic. Benthic waters were for the most part anaerobic to the sediment/water interface. Occasional oxygenation events allowed opportunistic benthic organisms to colonize the sea-floor. The aerobic/anaerobic boundary in the water column may have been located several millimeters above the sediment/water interface. Shells and sediment were not transported by bottom currents. The shells of benthic epibionts were preserved *in-situ*. Compaction of the Bituminous Shale occured prior to cementation of original porosity.

Summary of Diagenesis

The Bituminous Shale contains two main morphologies of pyrite which are the products of two stages of precipitation. The largely homogeneous mixing of the two textures of pyrite suggests that the formation of early framboidal and later euhedral pyrite was continuous. While diagenetic conditions were evolving with

depth, depositional conditions were constant during the formation of the Bituminous Shale.

Framboidal pyrite in the Bituminous Shale formed under anaerobic conditions while the sediment/pore water system was open enough to allow ample dissolved seawater sulfate to diffuse into the sediment and allow organic metabolic by-products and alkalinity produced during microbial sulfate reduction to escape.

Euhedral pyrite formed later in diagenesis as communication between pores became restricted during sediment compaction. Pyrite framboids provided a nucleous for the growth of larger euhedral crystals (Raiswell, 1982). Crystal growth was slowed by the restriction of sulfate replenishment, the lower availability of iron minerals, and the lower abundance and reactivity of the remaining organic matter.

Petrology of the Schlacken Lithology

The Upper and Lower Schlacken are thin (30 to 40 mm) clay-rich limestone beds within the Bituminous Shales (Figure 21). Schlacken beds occur throughout the Posidonienschiefer outcrop belt in southern Germany, and represent a regionally extensive depositional event (Kuspert, 1982). The Schlacken beds have been previously described (Kauffman,1981, Seilacher,1982) but the petrography has not been studied in detail.

Both Upper and Lower Schlacken beds are composed of Type II, microcrystalline allochemical rocks: clayey, pyritic biomicrosparites. Abundant illiite and organic matter give the rock an overall olive black (5 Y 2/1) color with flecks of black (N1) phosphatic fossils, and very light gray (N8) carbonate (Munsell Soil Color Chart, 1963). The rock is not fissile. In the field, weathered Schlacken often fractures along laminations which are marked by a concentration of fish and fossil debris.

A point count of a representative sample of the Schlacken (K74-16-25, Upper Schlacken bed, Upper Epsilon, Hauff Quarry) is reported in Table 3.

Organic matter is defined as red and brown amorphous material, excluding phosphatic fossils. Jet and bitumen are included in the organic matter category but did not occur as constituents in this sample.

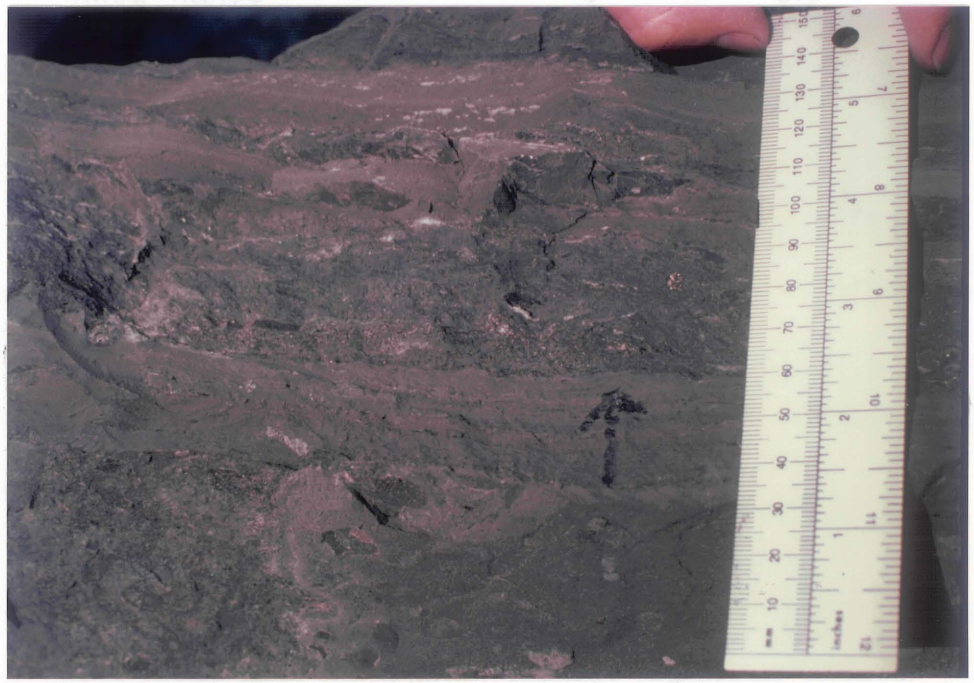


Figure 21. The Upper Schlacken extends from the 60 to 90 mm markings of the scale. The arrow indicates up direction. Note cross section of the belemnite guard near the 80 mm mark. Belemnite guards with geopetal cavity fillings are common in the Schlacken but not in the surrounding Bituminous Shale.

Constituent	Points	Percent
Clay Matrix	65	32.5
Quartz Silt	1	0.5
Mica flakes	0	0.0
Fossils	68	34.0
Spores	1	0.5
Organic matter	22	11.0
Spar	31	15.5
Framboidal Pyrite	9	4.5
Massive Pyrite	2	1.0
Plucked grains/Unknown	2	1.0
Total	**201**	**~100**

Fundamental End Members

Terrigenous	Allochemical	Orthochemical
33.0%	45.5%	21.0%
Error ± 3.2%	± 3.5%	± 3.4%

Table 3. Constituents and percent composition (by point-counting) of the Schlacken (Hauff Quarry, Holzmaden).

Mineral Composition.

Descriptions of each of the main constituents of the Schlacken lithology are presented as follows:

1. Terrigenous Minerals : clays and quartz.

2. Allochems: macrofossils, calcareous microfossils, spores, organic matter.

3. Orthochems: calcite, pyrite.

Clays

The clays were studied by X-ray Diffraction, petrographic inspection, and Scanning Electron Microscopy. The Schlacken contains 32.5, ± 3.5% clays. Calcareous nannoplankton are difficult to distinguish from the clay matrix in thin section. The range of error associated with determining the percent clay content by area may, therefore, be larger than reported above.

The clay mineralogy of the Bituminous Shale and the Schlacken is nearly identical. The clay minerals, listed in order of abundance, are illite, illite/smectite mixed layer clays, minor amounts of chlorite, kaolinite, calcite, and quartz (Figure 15). I infer that the source of the detrital clays was the same throughout deposition of the Bituminous Shale and the Schlacken.

Clay is less volumetrically important as a main constituent in the Schlacken than in the Bituminous Shale and is unevenly distributed between allochems. Most flakes are stacked on top of each other or lie at small angles to each other. SEM inspection reveals that clay orientation is unexpectedly jumbled compared to observations made by petrographic inspection. The jumbled

orientation could be the result of micro-bioturbation or, alternatively, cementation prior to complete compaction of the clay fraction. The lack of fecal pellets preserved in clay-rich areas or in microspar (discussed in more detail later) suggests that bioturbation was not a factor in the development of Schlacken fabric.

The color of clays in thin section is similar to that of clays in the Bituminous Shale (Pale Yellow Orange, 10YR 8/6 with tinges of orange). The clays exhibit slight pleocroism with the darker color in the North-South direction.

Although the clay mineralogy of the Bituminous Shale and the Schlacken are nearly identical, the clay fabrics of the two beds are distinctly different. As discussed previously, the orientation of clays in the Bituminous Shale shows evidence of slow and steady compaction and lack of bioturbation. In contrast, the clays of the Schlacken are oriented in face-to-face clumps or "domains" in a "flocculated fabric" (O'Brien,1987).

Fabric was studied by SEM inspection of fresh and acid etched rock surfaces. Fractured faces of the Schlacken were etched with 10% acetic acid for 2-5 minutes to disolve microspar which filled pore spaces between the clay flakes and allochem fragments. Figure 22 illustrates how much porosity of the unlithified precursor-mud was cemented by calcite microspar. The clays were cemented before they could orient uniformly parallel to the ocean floor and completely compact. O'Brien (1987) interprets the origin of this type of fabric to deposition of flocculated clay flakes unaffected by bioturbation.

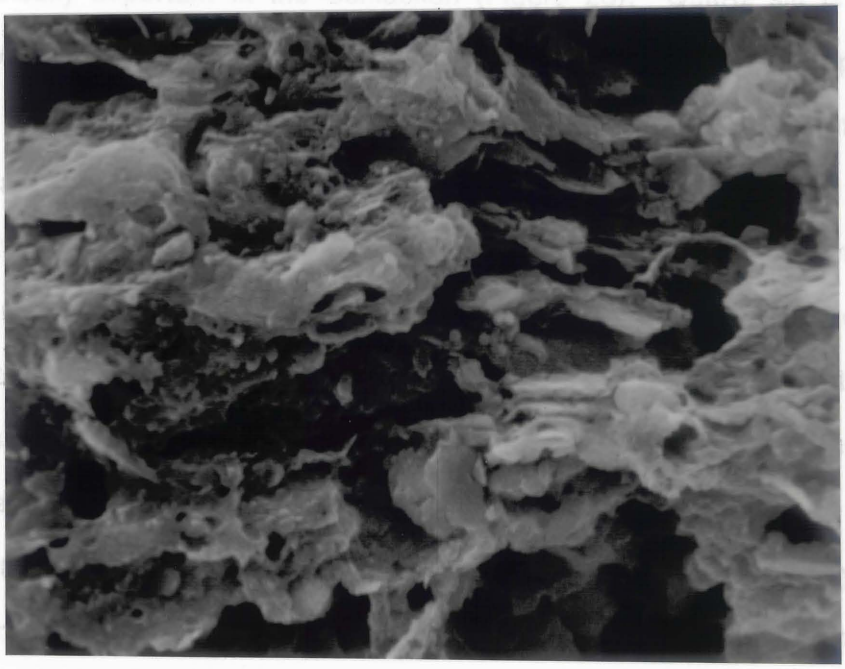


Figure 22. Acetic acid etched Schlacken. The acid has dissolved pore filiing microspar and revealed a jumbled clay fabric. Compare this figure to Figure 16 of the Bituminous Shale which illustrates a more compacted and well oriented clay fabric.

Quartz

Fine sand-size common quartz (0.15 - 0.18 mm diameter) and medium to coarse quartz silt (0.016 - 0.053 mm diameter) is common but not volumetrically important in the Schlacken (Figure 23). Quartz silt is randomly mixed with fossil fragments, organic matter and clays. As noted previously, aligned belemnite guards throughout the Schlacken indicate that currents periodically swept the sea floor. Therefore we would expect to find quartz silt distributed in starved ripples or at least lenticular wisps. In contrast, the ubiquitous and random distribution of quartz silt grains suggests deposition dominated by vertical, not horizontal, settling conditions. Settling from suspension, however, would produce graded bedding, for which there is no evidence. Since quartz silt represents such a low amount (0.5%) of the total rock composition, the significance of the conflicting evidence provided by analysis of the quartz fraction is minimized in interpreting the overall depositional conditions of the Schlacken.

Allochems

The Schlacken consists of between 30-40% fossils and fossil fragments, 11% organic matter, and 0.5% spores (Figure 24). X-ray analysis of bivalve mollusc shells which were separated from the matrix of Sample K74-2-21 detected only calcite.

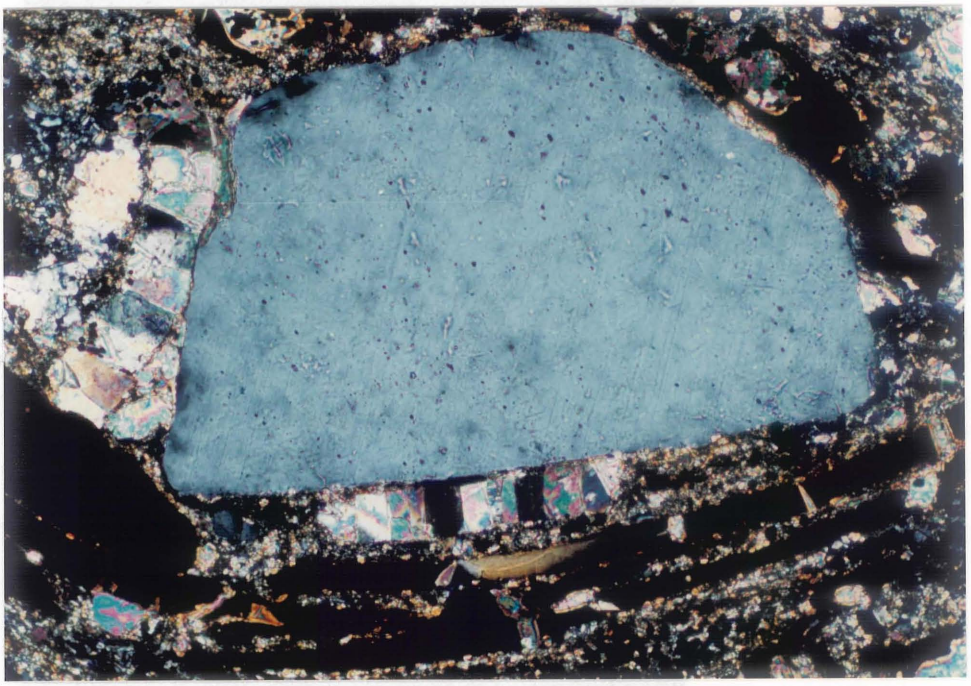
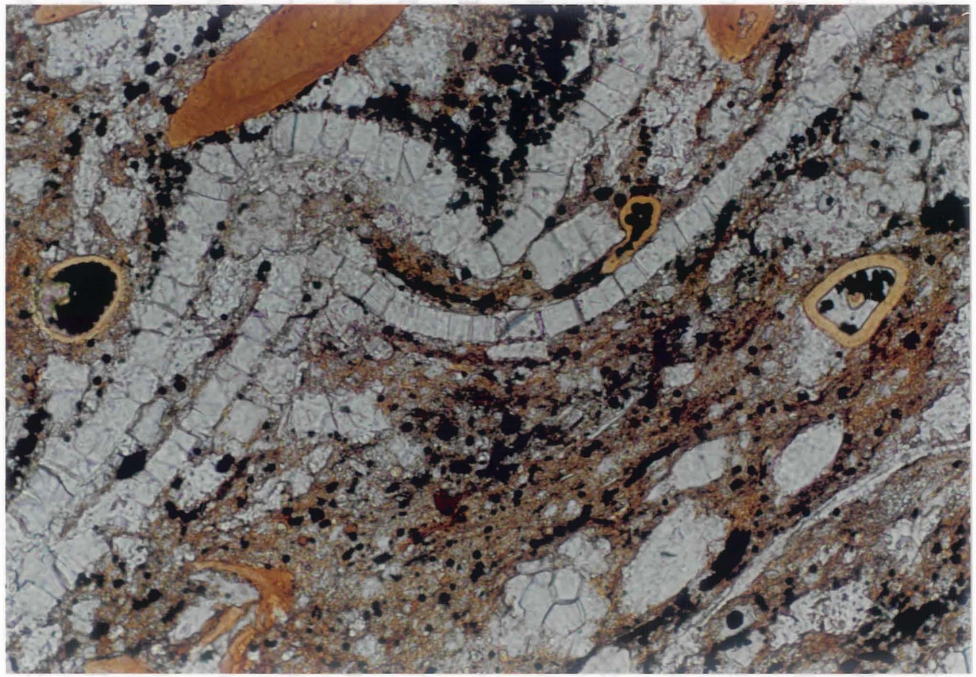


Figure 23. Quartz sand grain from the Schlacken. Photograph taken with cross-polarized light, magnification = 200X. The grain is 0.165 mm across. Note the calcite *inoceramus* prisms which abut the quartz grain at the left and bottom. Black areas are phosphatic fossil fragments. Microspar cements the surrounding clay matrix.

Phosphatic belemnite or fish fragment.

Pyrite-filled *Tasminites* spore

Prismatic calcite of *Inoceramus* and *Posidonia* fossils



Pyrite and calcite filled spore

Figure 24. Common types of fossils found in the Schlakcken. Magnification = 200X, field of view is 0.5mm wide.

Macrofossils.

The Schlacken contains abundant small (1-15 mm) calcite fossils, phosphatic belemnite and fish debris (<1 mm to 10 mm). Phosphatic fossils include belemnite hooks (Martill, 1986, and pers. comm.), fish bone fragments, and inarticulate brachiopod shells. Calcite fossils include *Inoceramus, Posidonia,* belemnite guards, and rare echinoid fragments. Only the prismatic calcite inner layer of *Inoceramus* and *Posidonia* shells are preserved. Larger allochems such as fish or belemnite fragments are generally oriented parallel to bedding, while smaller fragments of bivalves and other taxa appear to have no preferred orientation. *Inoceramus* and *Posidonia* shells in which the prisms are still articulated are oriented parallel to bedding. Some are warped and bent around adjoining fossils because of slight differential compaction of the surrounding sediment. Disarticulated calcite prisms from *Inoceramus* and *Posidonia* occur as jumbled masses and as individual grains within bedding planes.

The co-existence of shells with articulated prismatic layers and jumbled individual prisms of the same type of fossil is a textural inversion and suggests a complex depositional history. The living shell of *Inoceramus* and *Posidonia* was made of a nacreous aragonite inner ostracum and a prismatic calcite outer ostracum, both overlain by a periostracum made of conchiolin, a scleroprotein (Cox, 1969). No evidence of preservation of the nacreous aragonitic layers of *Inoceramus* or *Posidonia* was observed.

The presence of articulated prismatic calcite layers suggests that the shells were deposited while the periostracum was still in place, otherwise the prismatic

layer would disarticulate. The scattered prisms are too jumbled and randomly distributed to be the result of *in-situ* disarticulation of bedded shells. The jumbled prisms indicate post-mortem disarticulation and transport or winnowing by bottom current energy.

Most phosphatic fossil fragments were deposited as fragments. Some larger phosphatic shells have been deposited whole and subsequently broken *in-situ.* Intact *Inoceramus* shells predominatly lie flat in the bedding plane, but some are bent with undulating folds. This deformation is most likely the result of a small amount of sediment compaction during de-watering and not to post-mortem transport.

Belemnite guards are oriented parallel to bedding and aligned with a NNE paleocurrent direction as reported by Seilacher (1982). The abundant belemnite guards preserved in the Schlacken often have geopetal fillings in their hollow centers but the geopetal indicators do not have a consistent way-up orientation. No quantitative measurements of geopetal orientation were collected since the significance of the mixed indicators was appreciated only after leaving the field. Study of oriented museum slabs of the Schlacken at the University of Tübingen indicated that geopetal belemnite guards are distributed in a completely random orientation. The belemnite guards must have been deposited, and their cavities filled with geopetal sediment and spar, prior to their incorporation into the Schlacken. A sediment-stirring or transport event shifted the original depositional orientation of the guards and re-deposited them in their present mixed geopetal orientation.

The major source of the fossils which make up the framework grains of the Schlacken was reworked and winnowed Bituminous Shale sediment. The fossils in the Schlacken and the Bituminous Shale are identical in type but not in the proportion of total rock volume that they constitute. The Schlacken contains 34% allochems, while the Bituminous Shale contains 6%. As noted previously, the Schlacken has a low clay content compared to the Bituminous Shale. Clay deposition was either interrupted or clays were winnowed from the Schlacken. Current oriented belemnite guards indicate that bottom currents were active during Schlacken formation, therefore current winnowing is the mechanism most likely responsible for low clay content.

Microfossils.

Coccoliths and *Schizosphaerella* are common microfossils. Since the microfossils are so completely mixed with the clay matrix, it is difficult to point count or estimate their exact contribution to the carbonate fraction of the Schlacken. Filtering strong transmitted light with a white card helps in distinguishing coccoliths from microspar (Figure 25). Grün, Prins, and Zweili (1974) described 19 species of coccoliths and calcareous nannoplankton from the Posidonienschiefer at Holzmaden and estimated that in certain layers, coccoliths formed over 50% of the carbonate fraction of the rock.

Tasmanites spores are common but not volumetrically important throughout the Posidonienschiefer (B. Luguis, pers. comm., 1987). They are of special interest in the Schlacken, however, since they occur in their original spherical morphology with calcite cement, and occasionally framboidal pyrite,

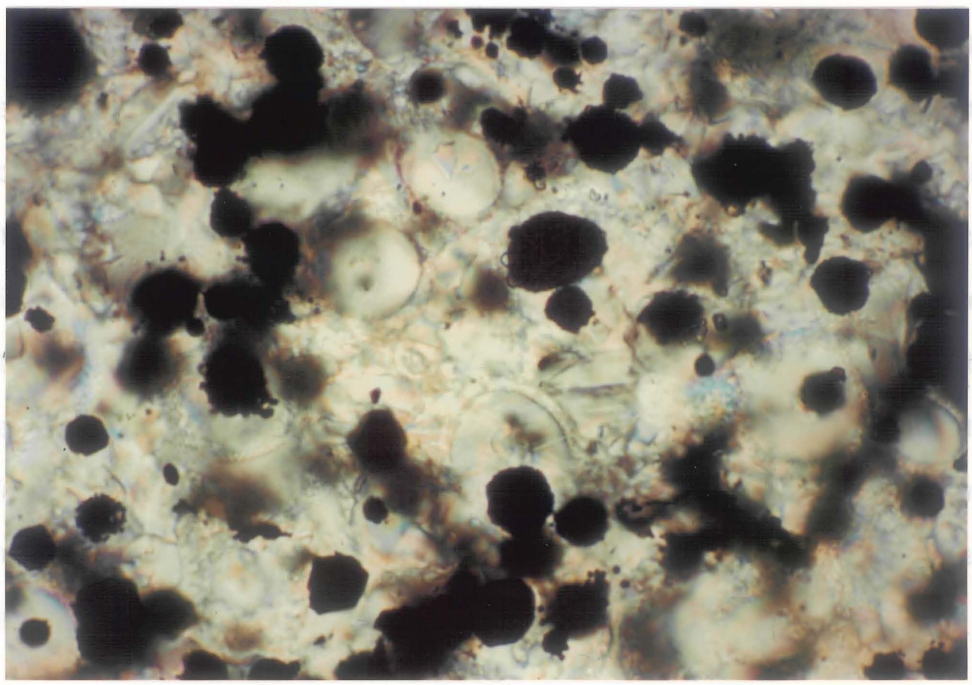


Figure 25. Photomicrograph of microspar-binding coccoliths and pyrite framboids together. Photo taken with modified White Card Technique, magnification = 1,250 X. Becke Lines from clay flakes interfere with the resolution of such small particles. The White Card Technique (described in text) filters out the Becke Lines. The microspar cement exhibits few of the criteria for cements identified by Bathurst (1975).

filling the interior void (Figures 24 and 27B). Spores in the Bituminous Shale occur with about the same frequency but are almost always preserved as flattened spheres with no internal authigenic minerals. Cementation of the spores in the Schlacken must have been very early in the diagenetic history in order to preserve the spherical morphology before the delicate spore was compacted.

Amorphous organic matter is ubiquitously distributed in the Schlacken, but not as abundantly as in the Bituminous Shale. Organic matter occurs in the Schlacken as bitumen, jet, and kerogen. Jet is rare and found only as the remains of driftwood fragments. Bitumen and kerogen are intricately mixed as amorphous organic matter and distributed in wisps and clumps throughout the Schlacken. My attempt to quantify the amount of amorphous organic matter by point counting resulted in a figure of 11±1 % (by area, not weight). Kuspert (1982) reported TOC for the Schlacken as less than 5% by weight (analytical method not reported). He analyzed the amorphous organic matter as 10% bitumen and 90% Type II kerogen, the same ratio as reported for the Bituminous Shale.

Orthochems

Calcite

The calcite cements provide the most interesting and important information about deposition and early diagenesis in the Schlacken. The cements provide information on the pore water chemistry during early diagenesis, the timing of cementation, and the microfauna of the sediment.

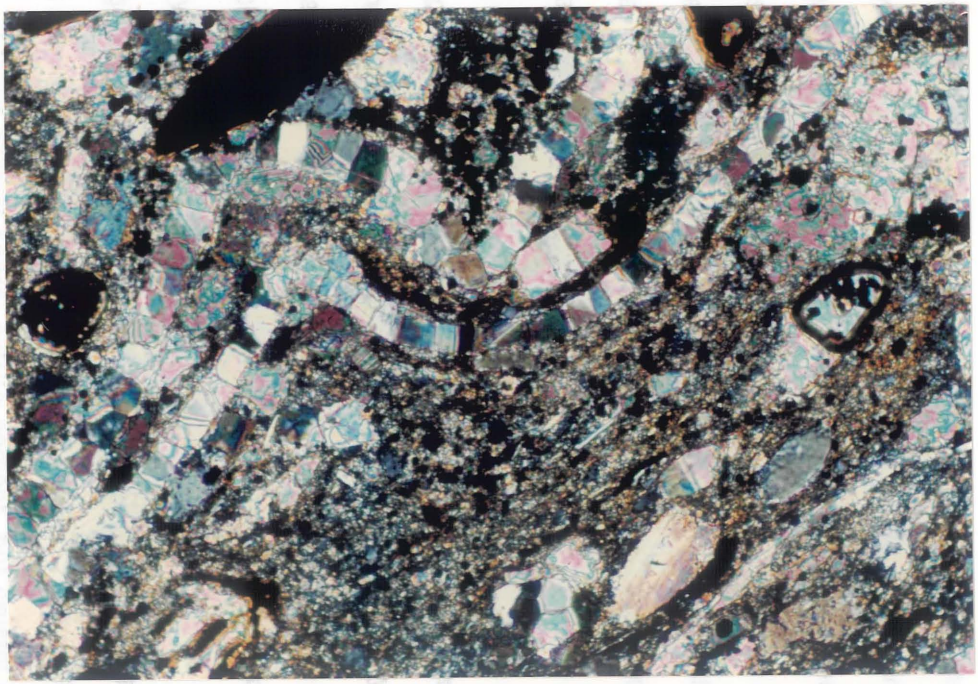


Figure 26. Same view as Figure 24, but in cross polarized light. Magnification = 200X, field of view is 0.5mm wide. Note the abundance of aphanocrystalline calcite between allochems and in the central clay-rich area. Close inspection suggests that the calcite is a microcrystalline cement, or "microspar".

Cement occurs in several morphologies, some of which are not commonly observed in sandstones or pure carbonate rocks. Pores in which cement may form are very small. Sparry calcite formed soon after deposition in the holes of phosphatic fossil fragments and inside marine algal spores. Calcite micro-concretions and concretion bands formed with framboidal pyrite and trace amounts of organic matter. Microspar, usually thought to form as the replacement of micrite, may have precipitated directly, the crystal size being constrained to <10μm diameter by extremly small intergranular spaces between allochems and clay particles.

Cements were studied by petrography and SEM. All cements in the Schlacken are calcite; X-Ray Diffraction detected no aragonite. Microspar represents about 14%, and Normal Spar about 1.5% of the total spar in the Schlacken.

Microspar. Very fine calcite particles, 5-10μm in diameter, are mixed with amorphous organic matter and clay and exhibit poor crystal form (Figure 26). The aphanocrystalline (0.001 - 0.004 mm) calcite that is intimately mixed with clay, pyrite, and organic matter may have been deposited as mud and subsequently recrystallized (Folk, 1962), or may have directly precipitated as a cement (Wiggins, 1982). Clay flakes and other micro-allochems are analogues of sand grains in a sandstone. Calcite binding the clay particles in the Schlacken could be considered normal sparry calcite cement, but crystal size of pore filling cements are <10μm. Microspar may have precipitated directly in inter-clay particle pores as cement.

The aphanocrystalline microspar fits few of Bathurst's (1975) criteria for cements. No cements show fibrous crystals, and all seem to have formed in one generation. The microspar does show sharp contact edges with allochems. There are no geopetal cavities; cements fill all voids. Crystal sizes do not grade from small to large towards the center of voids; instead most pores are filled with a single crystal of cement. This may result from the effects of the extremely small pores and a rapid rate of cementation.

Microspar which forms by the neomorphism of micrite often retains shadows of precursor pellets and relict carbonate mud. Analysis using the White Card Technique (Delgado 1977, Folk 1987) indicates no relict mud or pellet shadows in the microspar. The lack of evidence for neomorphism of micrite supports the theory that the microspar precipitated directly as pore-filling spar. The lack of any relict fecal pellets also suggests that no burrowing organisms were present in the original muds, and the interpretation that toxic conditions existed in the sediment.

SEM analysis of fresh fractured surfaces of the Schlacken revealed poorly crystalline microspar binding allochems and clay flakes. Most crystal edges were obscured by clays and organic matter.

1-2μm diameter fossil bacteria are common as inclusions in the microspar. These inclusions are only visible when viewing the thin section with the Modified White Card Technique. The fossil bacteria and viewing technique are described in detail in the Fossil Bacteria section.

Sparry Calcite Cement occurs in holes in fossils (0.1 mm diameter), inside uncompressed algal spores (*Tasmanites*) (Figure 27 A and B), and in patches, often with phosphatic fossil fragments as inclusions (Figure 28 A and B). Crystals in these patches exhibit crenulated edges with embayments that mimic those found in volcanic quartz grains. These grains have strong undulose extinction, similar to stretched metamorphic quartz. No clastic nuclei are apparent. Spar also fills cracks in disrupted fossil fragments (Figure 27 C).

Rounded micro-concretions, concretionary wisps and bands form throughout the Schlacken (Figure 29). Within the normal jumbled matrix of the Schlacken, occasional pods of framboidal pyrite are cemented with microspar in morphologies that mimic larger normal carbonate concretions. 1 mm thick concretionary layers occur sporadically throughout both Schlacken beds, often near the contact with the Bituminous Shale (Figure 29 A and B).

Pyrite

Only framboidal pyrite is present in the Schlacken and occurs as isolated spheres and in lenses and aggregates (Figure 30). Framboid sizes range from 2-50μm with the 10-20μm size most common. Aggregates of framboids are common inside holes in fossil fragments. The large euhedral blebs of pyrite which form slowly during later diagenesis (Raiswell and Berner, 1980) and are common in the Bituminous Shale, are virtually absent from the Schlacken.

As discussed previously, anaerobic waters, an ample supply of sulfate, reactive iron, and reactive organic matter are necessary for syndepositional and

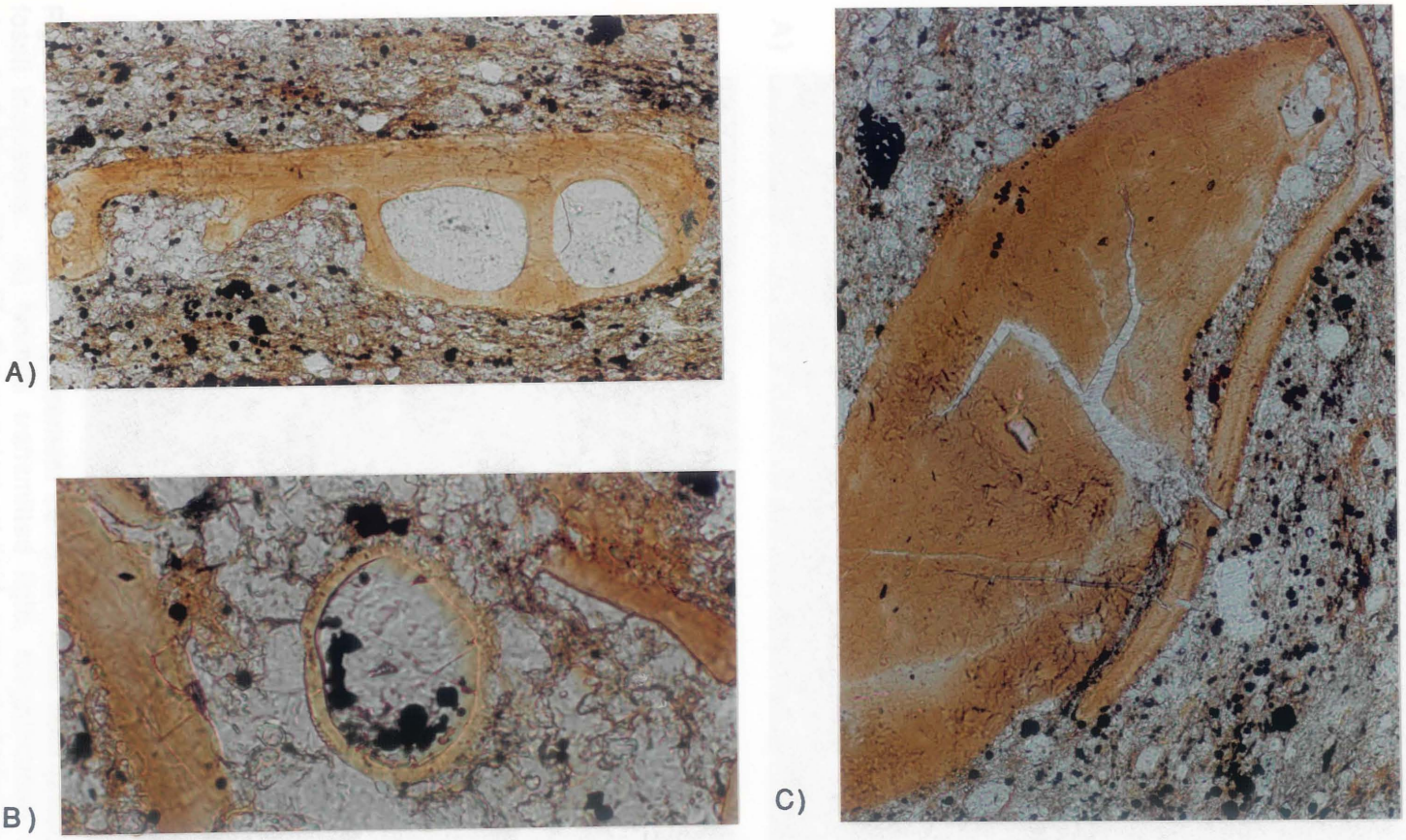
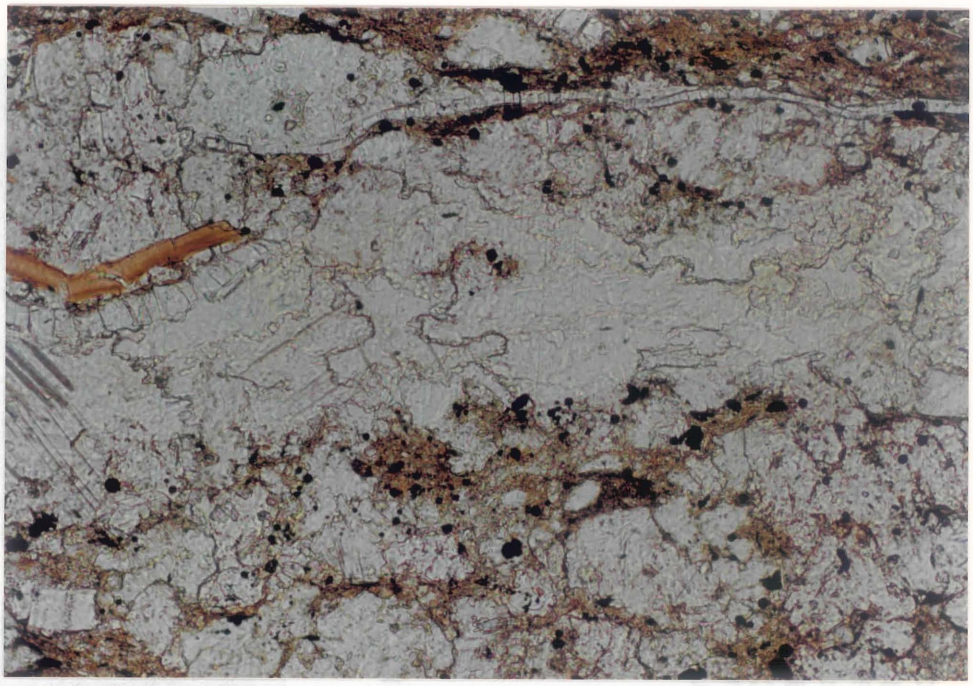


Figure 27. Occurrences of normal spar cement in the Schlacken. A) Spar filling holes in fossils. Magnification = 200X. B) Spar and pyrite framboids filling an uncompressed spore. Magnification = 400X. C) Spar filling cracked phosphatic fossil fragment. Magnification = 200X, field of view is 0.4 mm wide.

A)



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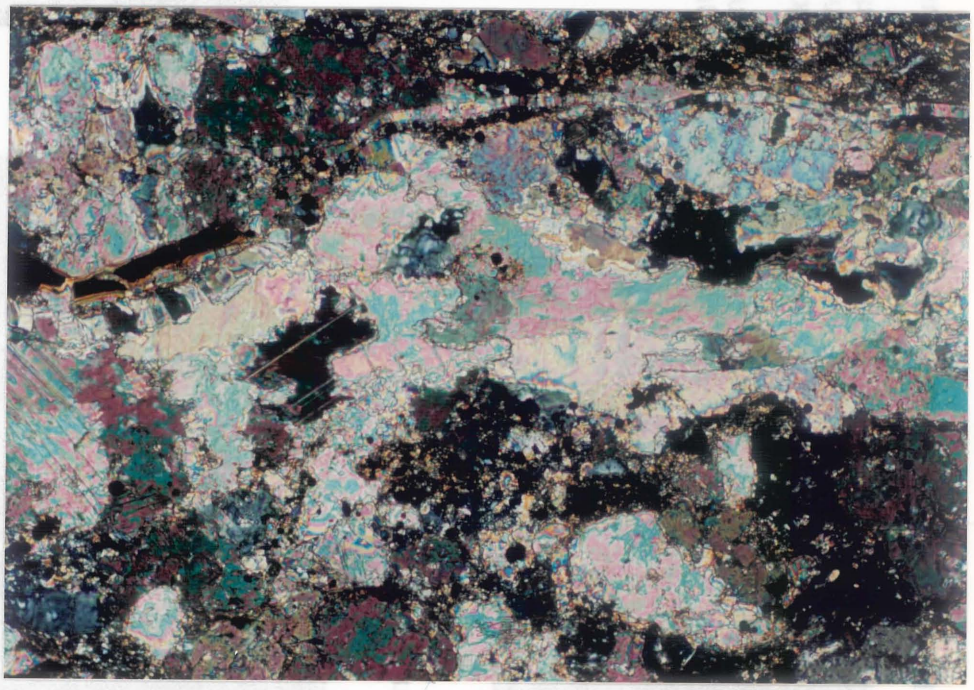
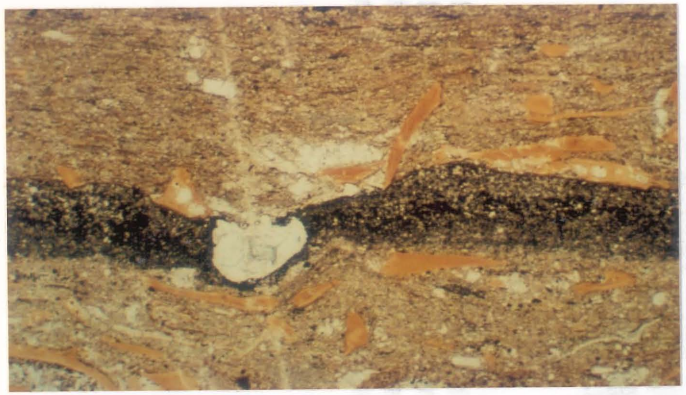
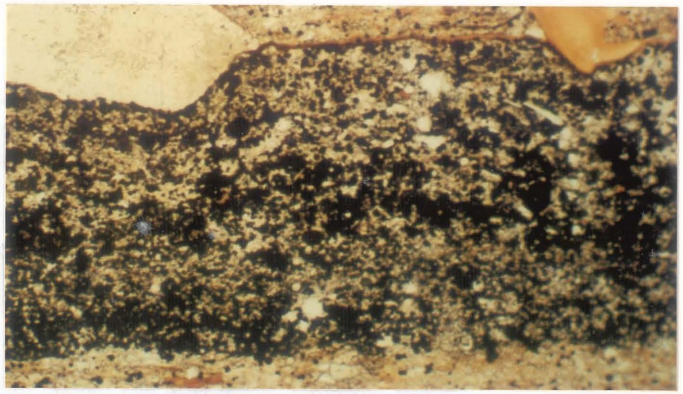


Figure 28. Later calcite replacement cements. Note both phosphatic and calcite fossil inclusions. A) Normal transmitted light, magnification = 200X, field of view is 0.5mm wide. B) Cross-polarized light, same magnification as A.

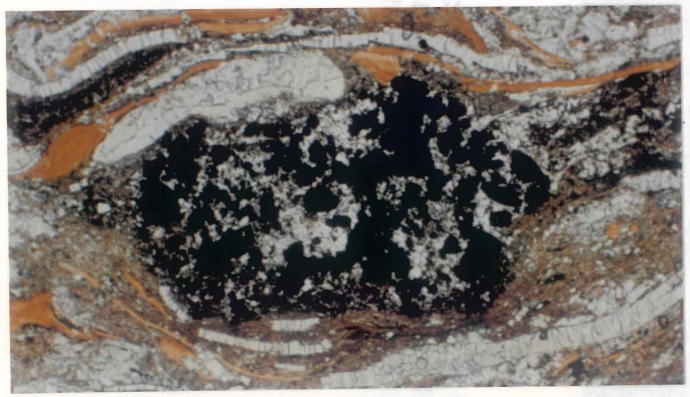


A) Magnification = 60X, Scale = 1mm.



Scale = 1mm.

B) Magnification = 100X,



C) Magnification = 40X, Scale = —— 1mm.

Figure 29. Two occurrences of calcitic concretions within the Schlacken.
A) Concretion band with large blebs of calcite filling voids. B) Close up of concretion band. Band is largely frambiodal pyrite and calcite cement.
C) Micro-concretion exhibiting usual rounded morphology of larger concretions.

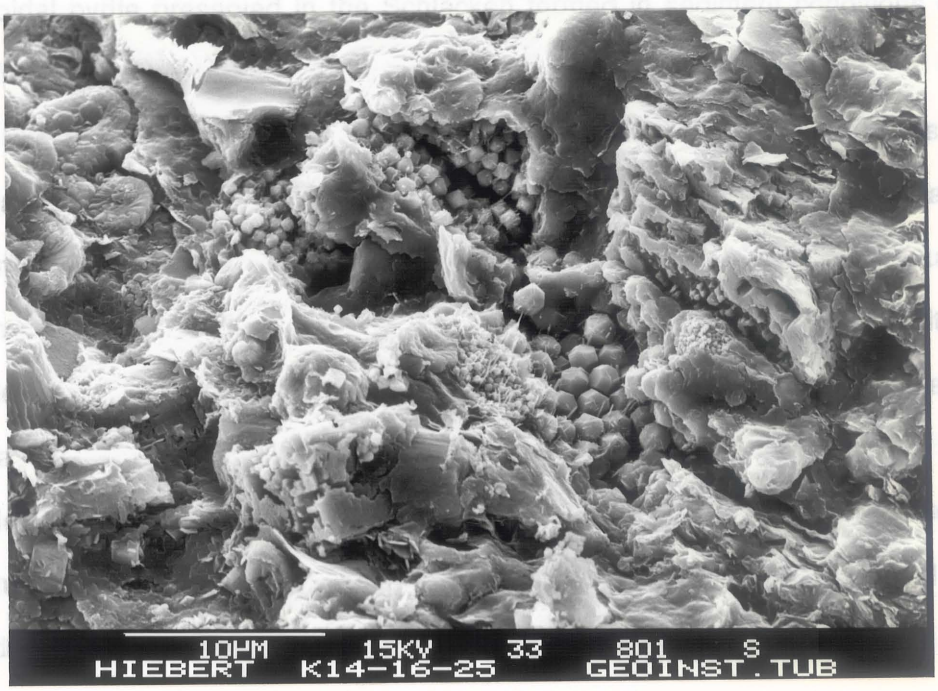


Figure 30. Framboidal pyrite in the clay/coccolith matrix of the Schlacken. Euhedral pyrite does not occur in the Schlacken. Note exposed coccoliths in upper left corner. Bedding plane extends from lower right to upper left of the micrograph. Scale bar = 10μm.

diagenetic pyrite formation. Framboidal pyrite forms in an open sedimentary system. Euhedral pyrite forms in a system with a restricted supply of sulfate and escape of bicarbonate. The constituents of the Schlacken sediment included ample iron-bearing clays, seawater sulfate and organic matter for pyrite formation. The framboidal pyrite preserved in the Schlacken formed in sediment conditions open to sulfate replenishment and diffusion.

The presence of primary pore-filling microspar, however, suggests that soon after initial framboidal pyrite formation, the pore system of the Schlacken became restricted. Bicarbonate produced from microbial sulfate reduction accumulated in sediment pores in high enough concentration to begin precipitation of calcium carbonate cements. Restriction of pore spaces can be caused by compaction or cementation. Since the Schlacken has been shown to have experienced little compaction, early occlusion of pore space by cementation seems the most likely mechanism for creating the restricted pore-water conditions recorded by the microspar cement.

Summary of Deposition and Diagenesis

The formation of the two Schlacken beds may be characterized in two stages: 1) A high energy current or storm event re-suspended a substantial amount of Bituminous Shale sediment and winnowed away clays and organic matter, leaving a porus lag deposit of fossil fragments and 2) early precipitation of diagenetic pyrite and calcite cement was initiated by a bloom of intense microbial activity.

As summarized previously, the Bituminous Shale was deposited in quiet, anaerobic conditions beneath shallow, highly productive warm seas. Sedimentary structures and current-oriented fossils indicate that a high energy event, most likely a combination of both storm generated waves and bottom currents, resuspended unconsolidated muds and winnowed away , or suspended, a portion of the clays and organic matter. Fossil fragments and authigenic minerals that were previously deposited in the muds settled from suspension and formed a porous fossil debris layer. The allochem framework of the Schlacken represents a lag deposit of winnowed Bituminous Shale sediment.

The sudden release of clay and buried organic matter from the resuspended sediment, and the high probability that the mixing event oxygenated bottom waters, created perfect conditions for a population explosion of aerobic bacteria. Bacteria degrade organic matter by enzyme-catalyzed oxidation-reduction reactions. Most bacteria must attach their cell wall to the organic matter they degrade in order for their internal and extenal enzymes to bind to organic substrates and function (Brock, 1974, p.100-131). The amount of surface area available on organic matter therefore, is a critical element in determining the ultimate activity and total chemical effect of bacterial populations on their environment. The sudden re-suspension of previously buried particulate organic matter and clay particles (often coated with organic matter) increased the available surface area for microbial attachment by orders of magnitude. The high demand for oxygen caused by the microbial oxidation of organic matter would have quickly and completely depleted the limited oxygen supplied by the mixing event.

Anaerobic conditions rapidly resumed and the remaining organic matter and clays slowly settled into an anaerobic porous sediment where sulfate reducing bacteria continued degradation.

Framboidal pyrite formation was rapid while the sediment was open to sulfate replenishment from communication with seawater. Bicarbonate alkalinity produced as a result of sulfate reduction could diffuse into the seawater as well. As the resuspended clays and organic matter gradually settled over the debris layer and normal depositional conditions resumed, pore water communication with the overlying seawater was gradually restricted, cutting off the supply of sulfate and allowing the bicarbonate concentration in the pores to reach supersaturation and begin precipitation of calcite cement. Early cementation preserved delicate algal spores and the flocculated "house of cards" fabric of the clays that remained in the fossil debris sediment.

The framework grains of the Schlacken bed were cemented in a manner similar to that of common rounded carbonate concretions, except that the rapid rate of early cementation preserved the entire layer as a concretionary bed. Curtis, Pearson, and Somogyi (1975) interpreted a concretionary siderite sheet, similar in many aspects to the Schlacken beds, in the Westphalian of Yorkshire, England, as having a microbially influenced diagenetic origin. As in the Schlacken, the concretionary layer consisted of larger framework grains than the surrounding organic-rich shale and included a profusion of framboidal pyrite cemented by carbonate. The authors concluded that the formation of early carbonate cement indicated the involvement of anaerobic bacteria, but did not

venture to suggest the mechanism by which the carbonate was precipitated. Raiswell (1971) described concretions from the Black Ven Marls of the lower Liassic near Lyme Regis, England which formed in sediment systems open to sulfate diffusion from seawater. They are rich in framboidal pyrite and are cemented by carbonate that has an isotopic signature (enriched in ^{12}C) which indicates that organic carbon was the source for carbonate precipitation. Raiswell's data also indirectly implicates bacteria in the precipitation of carbonate in concretions. Neither Curtis *et al.,* nor Raiswell inspected the concretions for the occurrence of bacterial fossils.

The production of bicarbonate from organic matter as a by- product of microbial sulfate reduction and the occurrence of bacterial bodies fossilized in the Schlacken cements suggests that bacteria played a significant role in altering the geochemical conditions in the restricted pore waters and may have initiated the precipitation of calcite cements.

Microbially Initiated Precipitation of Calcium Carbonate

The role of marine bacteria in the precipitation of calcium carbonate has been studied in the field by geologists (Ashirov and Sazonova 1962, Folk and Chafetz 1980, 1983, Chafetz and Meredith 1983, Chafetz and Folk 1984, Chafetz 1985, Folk, Chafetz, and Tiezzi 1985, and Folk and Tiezzi (in prep.)) and experimentally in the lab by geochemists and microbiologists (Drew 1911, Greenfield 1963, LaLou 1957, McCallum and Guhathakurta 1970, Berner 1968, 1969, 1971, Krumbein 1974, Morita 1980, Novitsky 1981, del Moral *et al.,*

1987). A complete exposition of the complex physical chemistry and biochemistry of this process is beyond the scope of this thesis, but a summary of the microbial mechanisms responsible for calcite formation in organic-rich muds and those aspects which pertain to the interpretation of the diagenesis of the Schlacken is presented.

The marine environment is ubiquitously populated by a wide diversity of aerobic and anaerobic detritus degrading (heterotrophic) bacteria. Since most bacteria must attach to a surface in order to function, a concentrated microbial community is found at the sea floor. Most heterotrophic bacteria have specialized on degrading one or several related biochemical compounds as food. A diverse community of specialized bacteria has evolved to degrade the complex association of organic molecules that make up animal and plant cells. The bacterial community acts in concert, each species or group of bacteria degrading a specific compound and passing the by-products on for further degradation by other specialists. Eventually the complex organic matter is degraded completely to CO_2 and H_2O, or microbial degradation is arrested at some point and the organic matter is preserved in the sediment.

Aerobic decay of organic matter occurs in the open water column or in open sediment/porewater systems. Acidic or basic products of microbial metabolism are rapidly buffered by seawater.

During the anaerobic decay of particulate organic matter, two important bacterial metabolic processes produce bicarbonate. As previously reviewed,

sulfate reducing bacteria oxidize organic matter to bicarbonate and reduce sulfate to sulfide:

$$SO_4^{=}{}_{aq.} + 2CH_2O \rightarrow H_2S_{aq.} + 2\,HCO^{-}{}_{3aq.} \quad (1)$$

The removal of sulfate, which acts as an inhibitor of carbonate crystallization by "poisoning" the crystal lattice, enhances the local environment for the development of calcite cement (Pigott and Land, 1986).

Complex organic molecules which contain nitrogen, such as amino acids and proteins, are degraded into ammonia and bicarbonate:

$$CO_{2aq.} + NH_{3aq.} \rightarrow NH_4^{+}{}_{aq.} + HCO^{-}{}_{3aq.} \quad (2)$$

In an open sediment-seawater system, bicarbonate will diffuse away from local concentrations into the open seawater reducing local bicarbonate alkalinity below the equilibrium carbonate ion product and thereby keeping carbonate in solution (Berner, 1971). However, if the microbial degradation of organic matter is occurring in a closed pore-water system, diffusion is restricted and the products of both reactions will build up high local concentrations in the sediment. The production and retention of ammonia in the sediment will tend to raise pH, thus favoring carbonate precipitation. Berner (1969) and Morita (1980) experimentally determined that during anaerobic microbial decay of marine organic matter in restricted conditions, pH of the sample waters rose above 8.5

and remained alkaline for the duration of experiments (8.5 months and 24 days, respectively). In restricted environments, bicarbonate concentration may exceed the equilibrium ion product for calcium carbonate and precipitation of calcite cement may begin. Bicarbonate will react with free calcium ions to form calcium carbonate as follows:

$$2\,HCO^{-}_{3aq.} + Ca_{aq}^{++} \rightarrow CaCO_3 + CO_{2aq.} + H_2O \qquad (3)$$

Seawater and the dissolution of biogenic carbonate provides the source of free Ca^{++} ions for the formation of $CaCO_3$.

The production of organic acids as a by-product of microbial degradation of organic matter in addition to the CO_{2aq} formed in the above reaction will have the effect of acidifying the sediment pore waters and inhibiting carbonate precipitation. Berner (1971) points out, however, that the rate of base production (ammonia and bicarbonate) versus the rate of acid production in the local restricted environment is the factor which ultimately controls whether calcite precipitates or stays in solution. Under sediment conditions where abundant nitrogen-rich organic matter is available, such as the deposition of a fresh fish carcass or, as in the case of the Schlacken, a sudden release of reactive organic matter from sediment stirring, the production of ammonia may outstrip acid production and interstitial calcite cements may precipitate.

Besides the obvious chemical role of providing bicarbonate and raising pH, bacteria may also contribute to carbonate precipitation by providing a discrete

point of Ca^{++} concentration and therefore a nucleation site for the growth of calcium carbonate crystals. Greenfield (1963) showed that marine bacteria concentrated Ca^{++} on their cell walls. Morita (1980) also described bacteria that loosely bound Ca^{++} with cell wall proteins. If free Ca^{++} ions are concentrated on a bacterial cell wall in the presence of high concentrations of bicarbonate, calcium carbonate may form via equation (3).

Morita (1980) described a microbial mechanism that produces calcium carbonate crystals on the exterior surface of bacterial cell walls. As the bacteria internally degrades organic matter, CO_2 is produced as a by-product and diffuses through the cell wall, out into the surrounding fluids. The CO_2 is available to combine with a base such as NH_{3aq} to form bicarbonate and ammonia (as in equation 2). As a final result, bicarbonate is locally available to combine with Ca^{++} ions bound to the cell wall and precipitate calcium carbonate. Once a single crystal of calcium carbonate is formed, it may act as a nucleation site allowing the rapid inorganic precipitation of a generation of cement. Krumbein (1974) observed the precipitation of aragonite on the surface of marine hetrotrophic bacteria in the presence of high concentrations of various types of organic matter. Morita (1980) and del Moral (1987) also found that marine and halophilic bacteria produced calcium carbonate crystals during laboratory experiments.

Bacteria appear to play both an indirect chemical role and possibly a direct physical role in the local precipitation of calcium carbonate. Under restricted anaerobic marine mud conditions sulfate reducing bacteria alter the local geochemistry of pore waters by producing bicarbonate and ammonia, and

diminishing the amount of sulfate. Bacteria that bind Ca^{++} ions to their cell walls act as nucleation sites for further precipitation of calcium carbonate. Bacteria that produce CO_2 and bind Ca^{++} to their cell walls may actively produce a crystal of calcium carbonate around themselves.

Figure 31 is a schematic model of how microbially initiated precipitation of calcium carbonate cemented the skeletal grains of the Schlacken during early diagenesis. The figure represents a snapshot in time, after the Bituminous Shale sediments had been re-suspended and the clays and organics were settling from suspension. The porous framework grains provided an open sediement/pore water system which allowed the rapid precipitation of framboidal pyrite. As clays settled on the Schlacken surface and restricted diffusion, sulfate reduction became the dominant microbial process. The pH of interstitial waters rose as ammonia and bicarbonate built up in the restricted pores. Ca++ binding bacteria may have provided nucleation sites for carbonate crystals precipitating from the bicarbonate saturated pore waters. Calcite cementation was rapid enough that delicate spores and fossils were preserved in three dimensions before compaction.

Fossil bacterial bodies trapped in the calcite cements confirms their presence during cementation. The discovery of fossil bacteria in the carbonate cements of the Schlacken is discussed in detail in the following section.

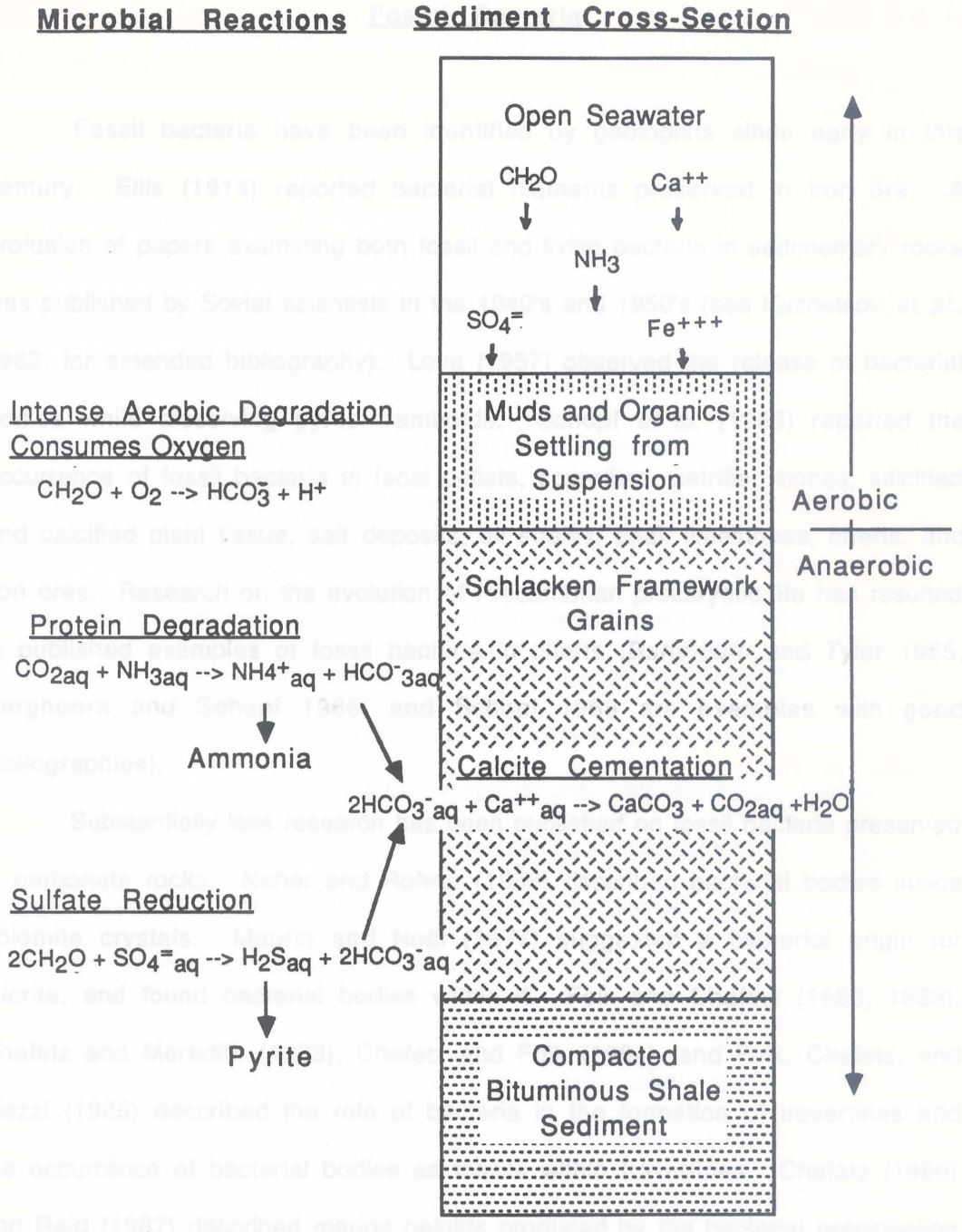


Figure 31. Schematic model of early diagenetic calcite cementation of the Schlacken. The process is described in detail in the text.

Fossil Bacteria

Fossil bacteria have been identified by geologists since early in this century. Ellis (1914) reported bacterial filaments preserved in iron ore. A profusion of papers examining both fossil and living bacteria in sedimentary rocks was published by Soviet scientists in the 1940's and 1950's (see Kuznetsov *et al.*, 1963, for extended bibliography). Love (1957) observed the release of bacterial bodies while dissolving pyrite framboids. Schopf *et al.* (1965) reported the occurrence of fossil bacteria in fecal pellets, coprolites, petrified bones, silicified and calcified plant tissue, salt deposits, oil shales, coal, limestones, cherts, and iron ores. Research on the evolution of Precambrian procaryotic life has resulted in published examples of fossil bacteria in cherts (Barghoorn and Tyler 1965, Barghoorn and Schopf 1966, and Schopf 1968 are examples with good bibliographies).

Substantially less research has been published on fossil bacteria preserved in carbonate rocks. Neher and Rohrer (1958) described bacterial bodies inside dolomite crystals. Maurin and Noël (1977) suggested a bacterial origin for micrite, and found bacterial bodies within it. Folk and Chafetz (1980, 1983), Chafetz and Meredith (1983), Chafetz and Folk (1984), and Folk, Chafetz, and Tiezzi (1985) described the role of bacteria in the formation of travertines and the occurrence of bacterial bodies as fossils within travertines. Chafetz (1986) and Reid (1987) described marine peloids produced by the bacterial precipitation of calcite. Tiezzi (1984) and Tiezzi and Folk (in prep.) described Paleozoic

vacuole-rich cements formed by the inclusion of bacteria in calcite crystals. Folk (1986, 1987) proposed that gray colored carbonate nodules in the famous black Portoro Limestone are the result of local bacterial diagenesis. (See Tiezzi and Folk (in prep.) for an extensive bibliographic listing of papers concerned with bacteria and carbonate rocks).

Microbiologists investigating the role of bacteria in the precipitation of calcium carbonate have reported bacteria trapped in the center of carbonate crystals formed during laboratory experiments. Oppenheimer (1961) suggested that bacteria formed spherical aragonite bodies in Bahama Bank muds. McCallum and Guhathakurta (1970) noted bacterial bodies forming the nucleus of aragonite needles precipitated from nutrient-enriched seawater solutions. Krumbein (1974) found that marine heterotrophic bacteria which precipitate aragonite, Mg-calcite and monohydro-calcite under both aerobic and anaerobic conditions were first coated, and then encapsulated with carbonate. Krumbein noted that the actual cells were destroyed by later crystal growth. Morita (1980) and del Moral *et al.*, (1987) also reported bacterial bodies incorporated in carbonate precipitated from nutrient enriched seawater in laboratory experiments. Ferris, Fyfe, and Beveridge (1988) have proposed a geochemical mechanism for the fossilization of individual bacteria based on experiments with *Bacillus subtilis* grown in a solution saturated with iron and colloidal silica. Metal cations (Fe++) were bound to the negatively charged bacterial cell wall and inhibited the production of enzymes (autolysins) which degrade the cell wall during growth. Silica from the saturated solution infiltrated pores of the cell wall and silicified

the cell structure. Experimental studies of bacteria in geological environments hold great potential for solving questions of microbial fossilization and microbially initiated diagenesis.

The study of thin-sections at very high magnifications with the petrographic microscope is the oldest and most commonly utilized method to identify fossil bacteria (see Kuznetsov *et al.*, 1963, Folk and Chafetz 1980, 1983, Chafetz and Meredith 1983, Chafetz and Folk 1984, and Folk, Chafetz, and Tiezzi 1985 for illustrated examples). Scanning electron microscopy of thin-sections, fractured rock surfaces, isolates of macerated rocks, and carbon-replicas of rock surfaces can substantiate and extend petrographic observations (Schopf, Barghoorn, Maser, and Gordon, 1965, discussed SEM sample preparation). X-ray and CAT scan analysis has also been employed in searching for fossil bacteria. Smith (1985) X-rayed shale and described fossils that resembled bacteria. Since the mid-1970's few attempts have been made to chemically analyze the content of bacterial "fluid inclusions" or analyze the fossil components (Nagy and Zumberge 1976, Williams 1984).

However, criteria for the unequivocal identification of fossil bacteria have not been widely accepted by the geologic research community. Because a tremendous diversity of bacteria inhabit modern sedimentological environments, comparison of the morphology of fossil and living bacteria is the most common method of identification.

There are three basic cell forms in living bacteria: Coccus - ellipsoidal or spherical (0.5 -1.0μm diameter), Bacillus - rod shaped (0.5 μm diameter, 1.5

μm long), and Vibrio - curved rod or spirillium (1.5 μm diameter to 13.0 μm long). Morphologies of colonies include : Sarcina - sheets of cocci, Trichomes- filaments of bacillus and vibrio in transverse directions, and Filaments- long strands of individual cells linked end to end by an encompassing cell membrane sheath (Tappan, 1980, p. 11). Geologists who use optical methods to identify fossil bacteria rely on these dimensions as guidelines.

Kuznetsov *et al.* (1963), Schopf, *et al.* (1965), Fairchild, Schopf, and Folk (1973), Cloud and Morrison (1980), Chafetz and Folk (1984), and Folk, Chafetz, and Tiezzi (1985), described fossil bacteria identified in petrographic thin sections by comparison with size and shape of modern bacteria. Schopf, *et al.* (1965), Chafetz and Folk (1984), Folk, Chafetz, and Tiezzi (1985), and others complemented their petrographic identifications with scanning electron microscopy.

Nagy and Zumberge (1976), and Williams (1984) combined petrographic, SEM, and geochemical analysis (mass spectrometry of organics, and nitrogen isotopes, respectively) to identify 1-2μm organic inclusions as fossil bacteria. Nagy and Zumberge described coccoid, rod, and lens-shaped fossils in the Precambrian carbonate Bulawayan stromatolites of Rhodesia. Williams documented filamentous bacteria-containing granules of elemental sulfur in the Miocene Monterey formation of California. Future work to identify fossil bacteria unequivocally will undoubtedly rely on a combination of petrographic and advanced geochemical analysis.

As geochemical signatures of modern bacteria that are active in sedimentological environments are identified, perhaps analysis of these "biomarkers" will provide another accurate method to identify fossil bacteria. White (pers. comm. 1986,1987) suggested analyzing suspected fossil bacteria for respiratory quinones and diglycerides (degraded phospholipids which still have typical bacterial fatty acids) with an ion bombardment mass spectrometer.

The identification of fossils as bacteria (versus cyanobacteria, algae, and fungi) is not easy, and taxonomic classification of fossil bacteria represents an even more difficult problem. Living bacteria are classified primarily on the basis of their biochemical behavior, which may leave distinctive remains (biomarkers) in the rock record. The geomicrobiologist working on fossil bacteria has only incomplete morphology and indirect geochemical evidence to judge taxonomic affinities. Most detailed taxonomic classifications of fossil bacteria, therefore, are of dubious value.

Criteria used in this investigation to identify fossil bacteria include analysis of size and shape, and analogy to the morphology of similar modern bacteria. Indirect geochemical evidence in the form of authigenic minerals surrounding the fossils helped in determining the environment in which the bacteria were living during deposition of the host rock. The bacterial fossils have not yet been analyzed for residual organic matter.

Experimental Work

Experiments in bacterial taphonomy were conducted to help develop a model for the possible optical appearance of fossil bacteria, to see if bacteria could be incorporated into mineral crystals, and to see if experimentally produced crystal fabrics would compare with the fabrics observed in the Posidonienschiefer carbonate cements.

Cultures of mixed populations of living aerobic and facultative anaerobic hydrocarbon-degrading bacteria in a medium of nutrient enriched seawater (NSW) were allowed to desiccate on glass microscope slides. (NSW = 98.9% Filtered Gulf of Mexico seawater from Port Aransas, Texas, 1.0% $(NH_4)_2SO_4$, and 0.1% K_2HPO_4). The concentration of bacteria was approximatly 10^6 cells/ml of seawater in the final slide preparations (Figure 32). This concentration is close to what might be expected at a marine sediment surface in the presence of a large amount of detrital organic matter (Oppenheimer, pers. comm., 1987)

Each slide preparation was repeated four times to insure that observations were not unique. The two most successful techniques used for preparing bacteria slides are as follows:

Rapid Desiccation Method: Three drops of bacteria-seawater medium were spread on the center of an ordinary glass microscope slide. The slide was slowly passed over a 60 watt light for 30 seconds to several minutes and allowed to desiccate. Distilled water was used to etch away excess halite and seawater impurities from half the slide. Etching thinned the surface coating of bacteria and

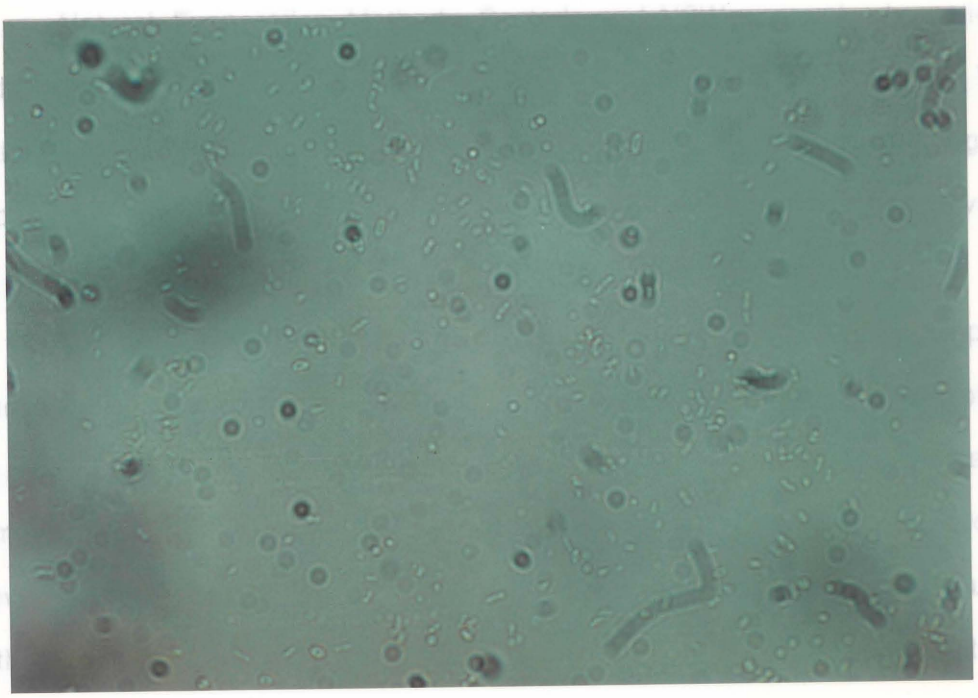


Figure 32. Mixed community of live hydrocarbon degrading bacteria in nutrient-seawater solution. Note the variety of rod and coccus shaped organisms. Cocci are 1-2μm diameter. The dark, blurry, filaments are dust particles in the seawater.

dried seawater to several microns thick, thin enough to expose individual bacteria and to etch individual halite crystals. This method provided good views of dried bacteria, but the evaporation rate was too fast to precipitate well-formed halite crystals.

Natural Evaporation Method: Bacteria and NSW were mixed, applied to slide surface, and allowed to evaporate at room temperature over two days. Well-shaped salt crystals (perfect hoppers) formed across the slide. No etching was necessary to observe crystals coated with bacteria. Bacteria also were observed to be trapped within the halite crystals.

For petrographic viewing at oil immersion magnifications, a cover slip was glued by the corners over the etched portion of the slide and immersion oil placed on top of the coverslip (oil placed directly on the etched bacterial medium remoistened the bacteria and allowed them to swim or be swept out of the field of view). Oil immersion microscopy was successful with the etched samples, but not with the naturally evaporated samples. The larger crystals in the naturally desiccated samples hampered the close objective distance necessary for oil immersion work. The oil also obscured the slight difference in refractive index between the salt and the bacteria which made observation difficult. Dry slide microscopy on large crystals yielded much better resolution.

Halite crystals up to a millimeter thick were formed at the edges of slides prepared with the natural evaporation technique. As the seawater solution evaporated, some bacteria were caught up in the halite crystal as is grew. Most bacteria were excluded from the crystals and concentrated as a film on the slide

surface. The glass surface of these slides provided a visual reference of the size and shape of dessicated bacterial bodies for comparison to bacteria caught up in the halite crystal itself. Photomicrographs of several large halite crystals are presented with the plane of viewing focused at three distinct levels within the crystal (Figures 33, and 34A and B). Bacterial bodies are preserved throughout the crystal, not just on the crystal surface. Scanning Electron Micrographs of halite crystals from the same preparations illustrate how the bacterial bodies are caught up in tiny negative crystals and incorporated into the halite during crystal growth (Figures 35 and 36).

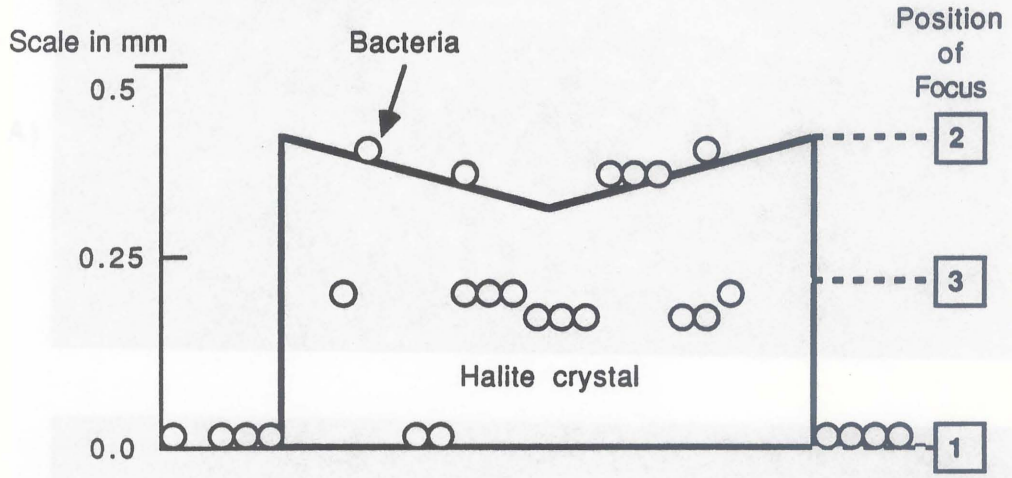
In these experiments, bacteria maintained their size and shapes despite heating and desiccation. Bacteria oriented along surface features of the individual crystal upon which they attached, but were not incorporated in regular patterns into the whole crystal. Some negative crystals contained bacteria.

Bacteria were incorporated along halite crystal edges within halite crystals. The experimental fabric of bacteria trapped in and around halite crystals was remarkably similar in appearance to the fabric observed in the Posidonienschiefer calcite cements.

Fossil Bacteria in the Schlacken

Populations of minute (1-2μm) spheres, rods, and chains of spheres were discovered trapped within calcite cements of the Schlacken. The cements are cloudy with inclusions and occur inside fossil spores, in cavities of fossil fragments, and in patches (as microspar) throughout the Schlacken. The most

The following series of three photomicrographs are of halite crystals which formed by normal evaporation of a solution of nutrient-enriched seawater and hydrocarbon-degrading bacteria. These photos were taken through a petrographic microscope with normal transmitted light. Magnification = 1,250 X. The following diagram illustrates in cross-section the plane of focus of each of the following photomicrographs.



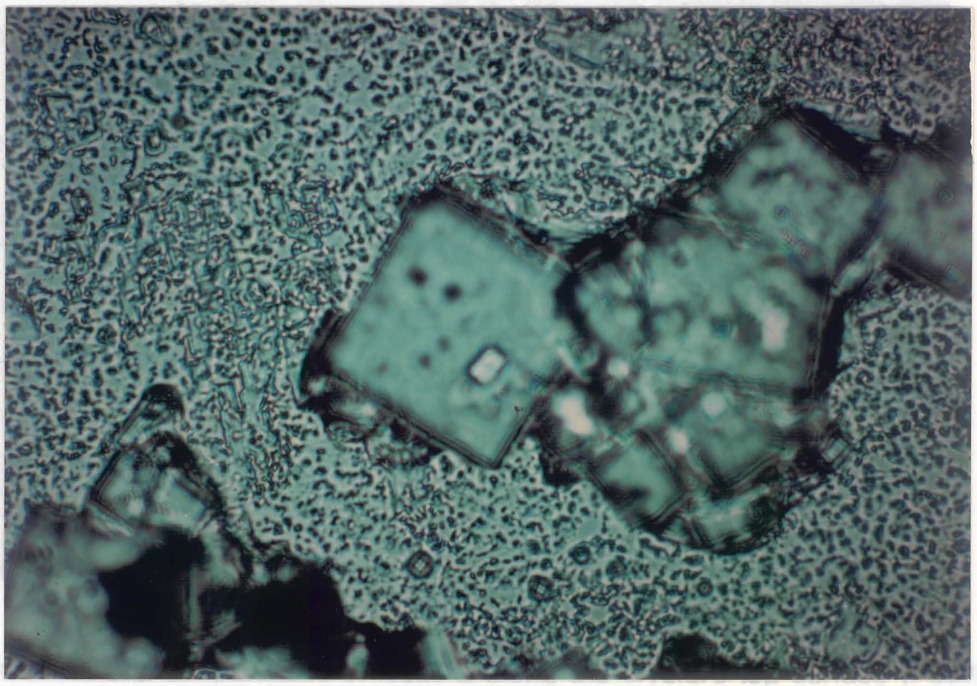
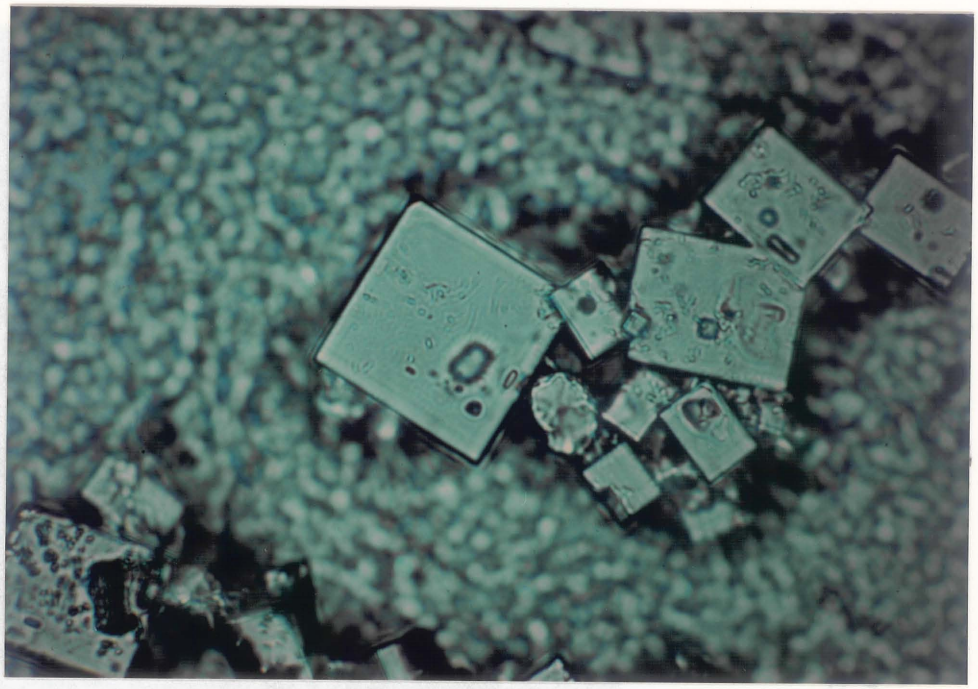


Figure 33. The plane of focus is along the surface of the glass slide (Position 1) and shows dense packing of bacterial bodies. The bodies are "fixed", ie., their muco-protein cell wall covering is dried onto the glass.

A)



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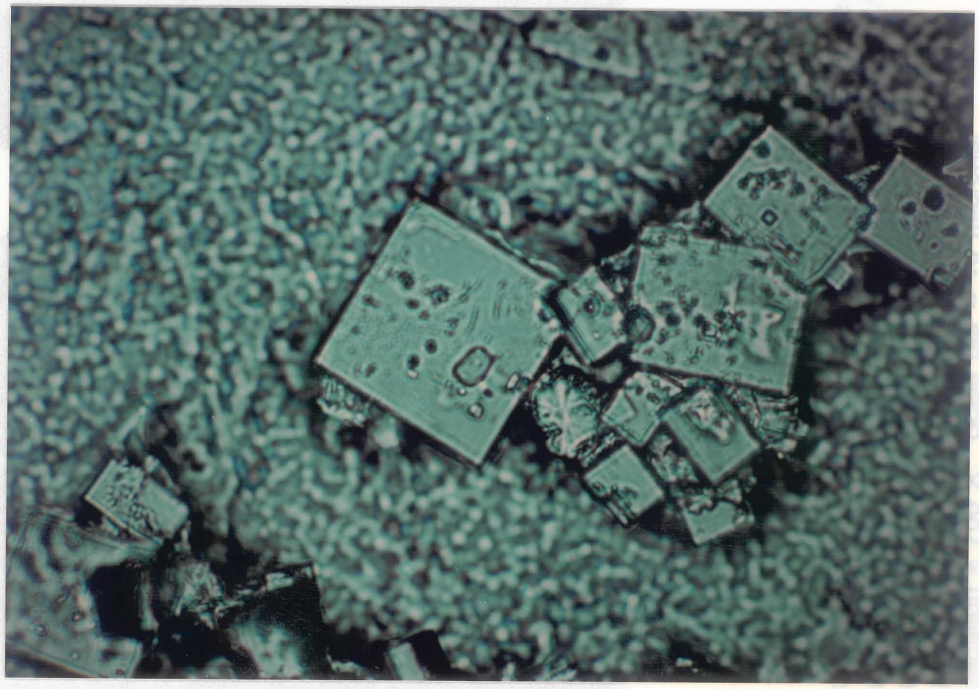
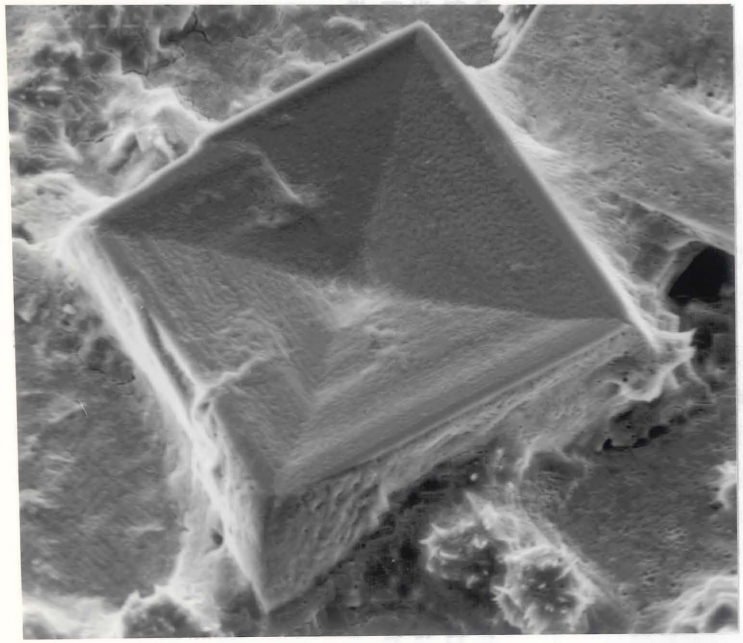
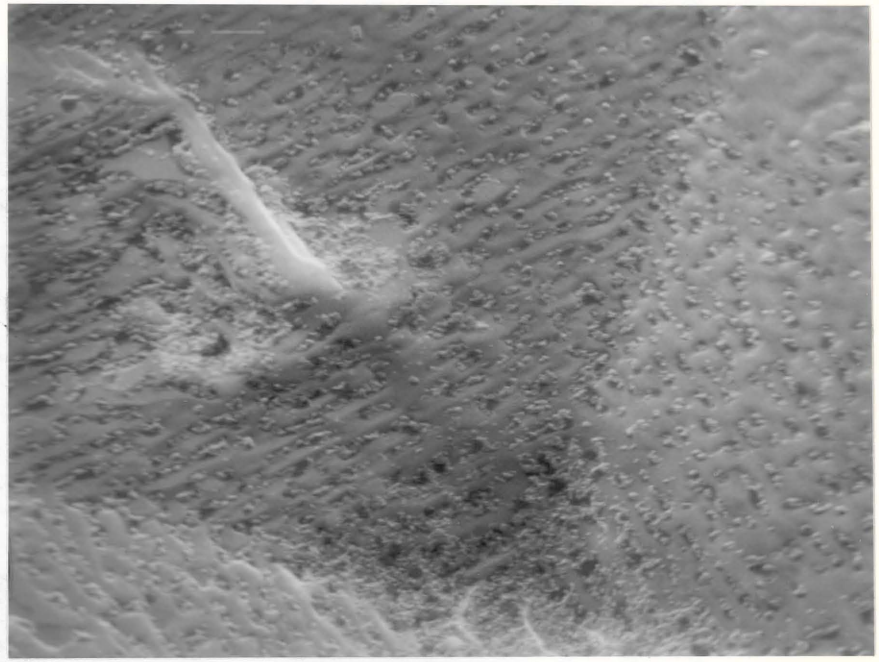


Figure 34 A and B. (A) Plane of focus is along the crystal's top surface (Position 2). Note both rod and coccus shaped bacteria on the crystal surface. (B) Plane of focus is through the center of the crystal (Position 3). Individual cocci, rods, and streptococci are in focus indicating that they are preserved within the salt crystal.



A)



B)

Figure 35, A and B. These SE micrographs show halite crystals formed from bacteria and nutrient-enriched seawater solution by the Natural Evaporation method (as described in text). (A) A well formed "salt hopper" crystal, about 4mm across. Magnification 200 X. (B) Close up of center portion of the crystal in (A). Note the profusion of one to two micron particles coating the crystal surface and concentrating in the runnels oriented at 45 degrees from each hopper axis. Magnification = 700 X. Scale bar = 10 microns.

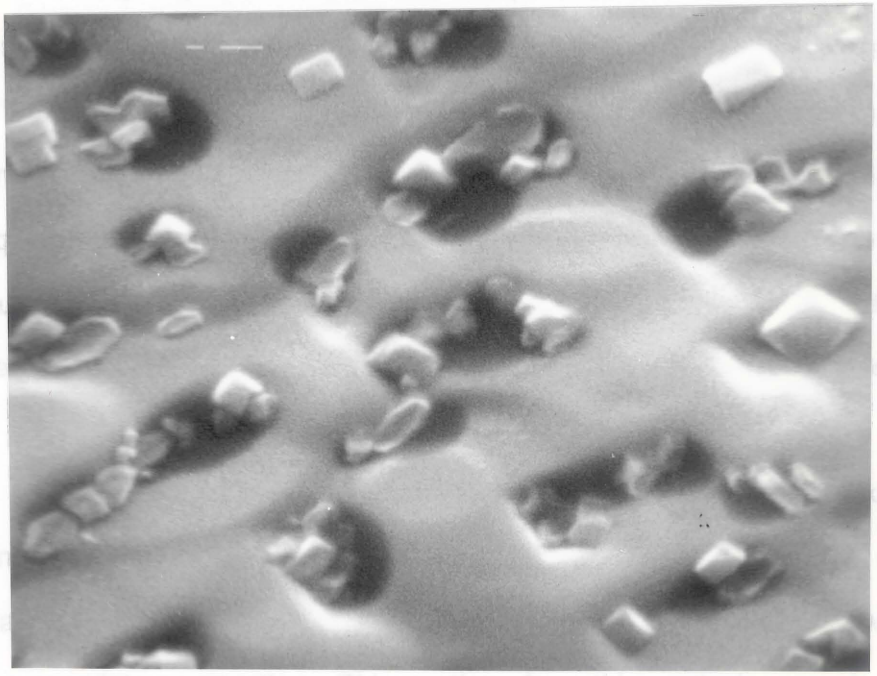


Figure 36. Closer view of the crystal face in Figure 35. 1-2μm long desiccated and deflated bacterial bodies of various morphologies are concentrated along crystal face runnels and in negative crystal holes. Microcrystals on the halite surface are impurities from the nutrient seawater. Magnification = 5,300 X. Scale bar = 1μm.

obvious fossil bacteria are preserved in unusual void-filling cements associated with a laterally continuous, 1.0 mm thick concretionary band.

Routine inspection of petrographic thin-sections led to the discovery of fossil bacteria. Duplicate slides of fossiliferous areas were prepared for etching and SEM study. Special thin sections were polished to a thickness of 10 to 15 μm, about half that of normal thin sections. One edge of the sample was polished all the way to the slide surface, affording a tapered thickness ranging from 15 μm to <1μm. Fossil bacteria were clearly observed in the tapered area of thin sections. Opaque materials above and below the one micron diameter bacterial bodies obscured fossils in thicker sections of the slide. The chance of observing a fossil bacterium in a nomal 30μm thick thin-section of a clay-rich rock is low (Figure 37).

The laterally continuous concretionary layers within the Schlacken contain the most clearly visible examples of fossil bacteria. Three dimensional ammonites and algal spores preserved in the Schlacken indicate that this rock was lithified before complete compaction. Thin sections from this particular sample reveal the most accurate record of original depositional fabric.

The large white bleb lying along the top of the pyrite band shown in Figure 40 is a patch of calcite cement which is cloudy with fossil bacteria. This sample was prepared from rock located only12mm from the ammonite fossil in Figure 38, and includes a cross sectional view of the interface betweeen the Bituminous Shale (top) and Schlacken (bottom). The black pyrite and calcite band is horizontally continuous throughout the handsample (3,150 mm^2 of surface) along the

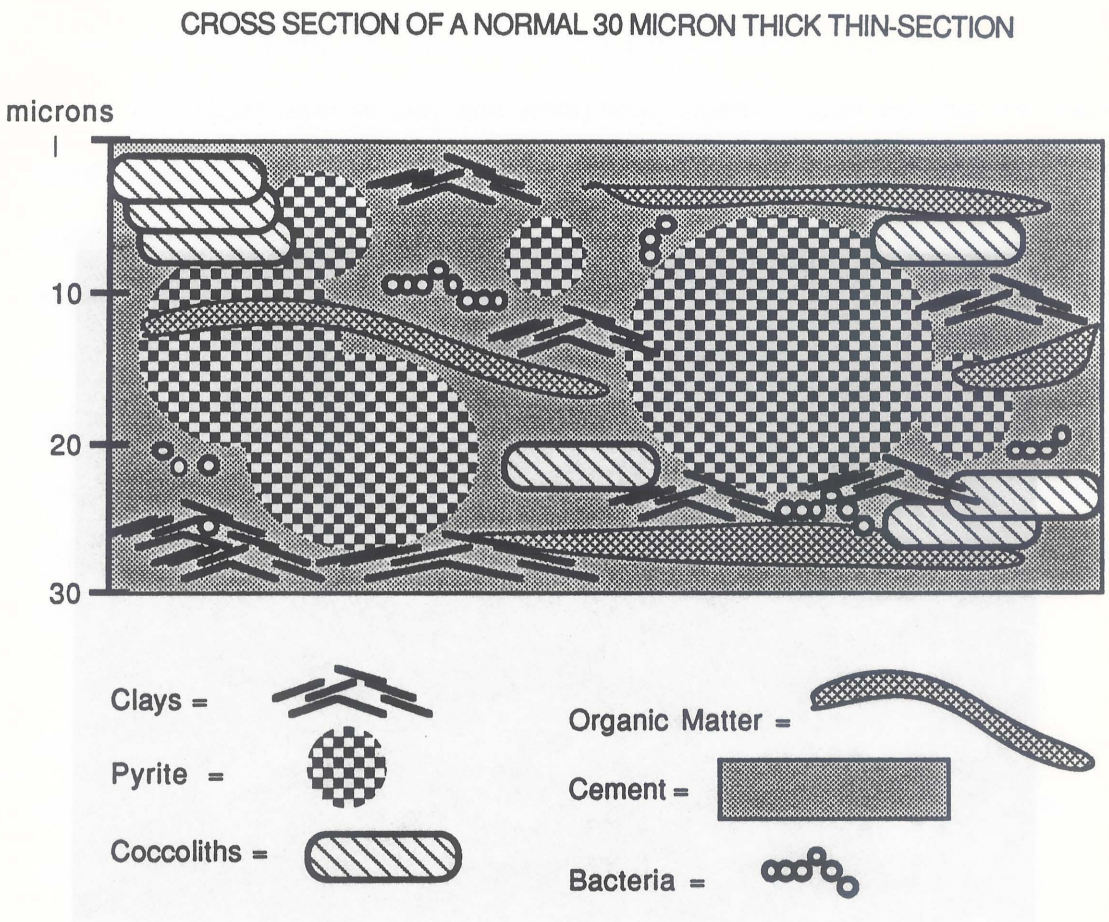


Figure 37. In a normal 30μm-thick thin section of a clay-rich carbonate, 1μm diameter fossil bacteria are most likely to be obscured by opaque constituents such as pyrite framboids, clay flakes, and amorphous organic matter.

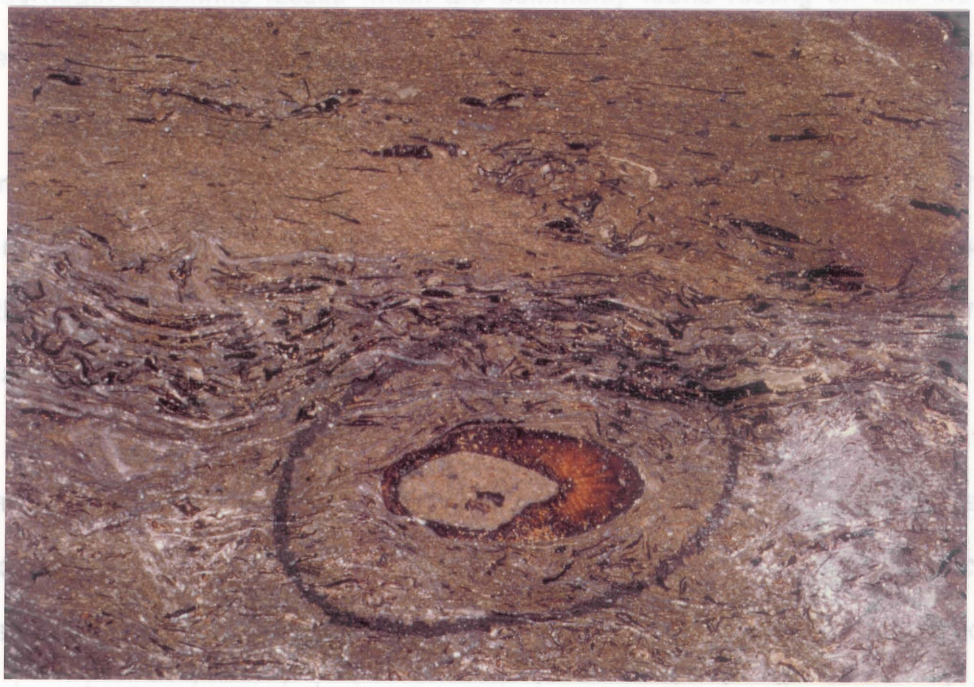


Figure 38. Polished hand sample of the contact between the Schlacken (bottom) and the Bituminous Shale (top). The circled ammonite is 8 mm long and is preserved in its original full-bodied shape indicating that the Schlacken has not undergone much compaction. Fossil bacteria were discovered throughout the Schlacken in various types of calcite cement.

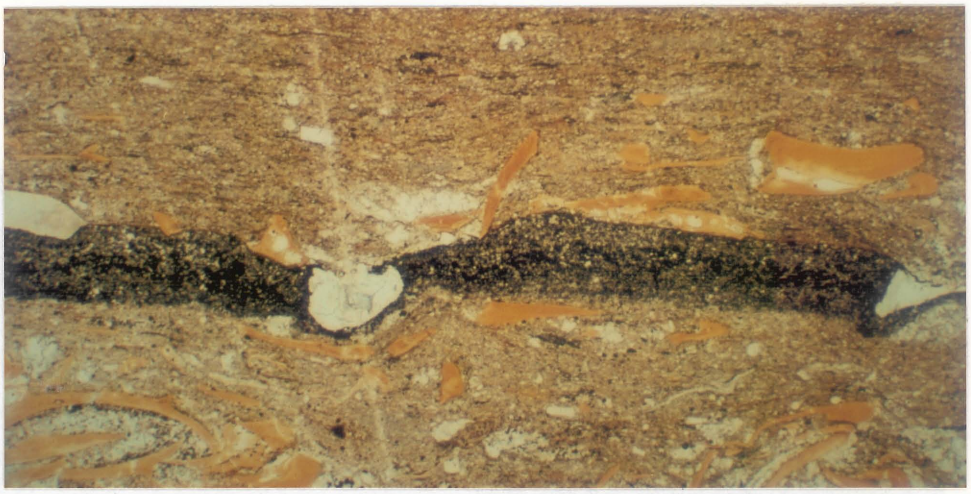
Schlacken/Bituminous Shale contact. The black components are framboidal pyrite, the white areas consist of coccolith and *Schizosphaerella* fragments, clay, organic matter, and rare quartz silt. The entire black band is cemented by calcite.

A 5-10μm layer of clay and amorphous organic matter overlies the black band lithology. This layer covers the top of the fossiliferous cement but passes underneath belemnite fossils which are commonly found resting on and indenting the black band layer (Figure 39B). The continuous lamina represents a physical or biological depositional event and a horizontal time line in the sample. The lamina serves as a boundary to separate constituents of the black band lithology from constituents of the overlying shale. The calcite cement blebs are associated with the Schlacken and the phosphatic fossils are associated with the Bituminous Shale.

Within the calcite cement blebs, the fossil bacteria are obvious at high magnifications (Figure 40). The fossils occur as 1-2μm diameter spheres, as short rods, and as strings of spheres linked together. The fossil shapes closely resemble the coccus, rod, and streptococcus morphologies of living bacteria. Various bacterial morphologies are noted among the fossils preserved in the calcite, but cocci predominate. Curving chains of spherical fossils closely resemble the common streptococci of modern marine bacteria (compare Figure 41A and B).

The bacterial fossils are randomly scattered throughout the cement and do not line up along crystallographic axes or along any perceivable crystal growth surface. The size and shape of the bacteria are remarkably uniform.

A)



B)

Figure 39 A and B. Two views of the unusual concretionary band in which void-filling calcite cements contain clouds of fossil bacteria. (A) Fossil bacteria occur in the calcite associated with the 1 mm thick band and in the microspar that cements the constituents of the band. (B) An enlargement of the calcite cement patch at the far left of (A). Framboidal pyrite appears as black spheres. Calcite fossil fragments and microspar appear as white patches. Clay is present but indistinct at this low magnification. Note the thin, continuous layer of rich brown clay and organic matter along the top of the concretionary band, which indicates that the calcite blebs are associated with the concretionary band and not the overlying sediment.

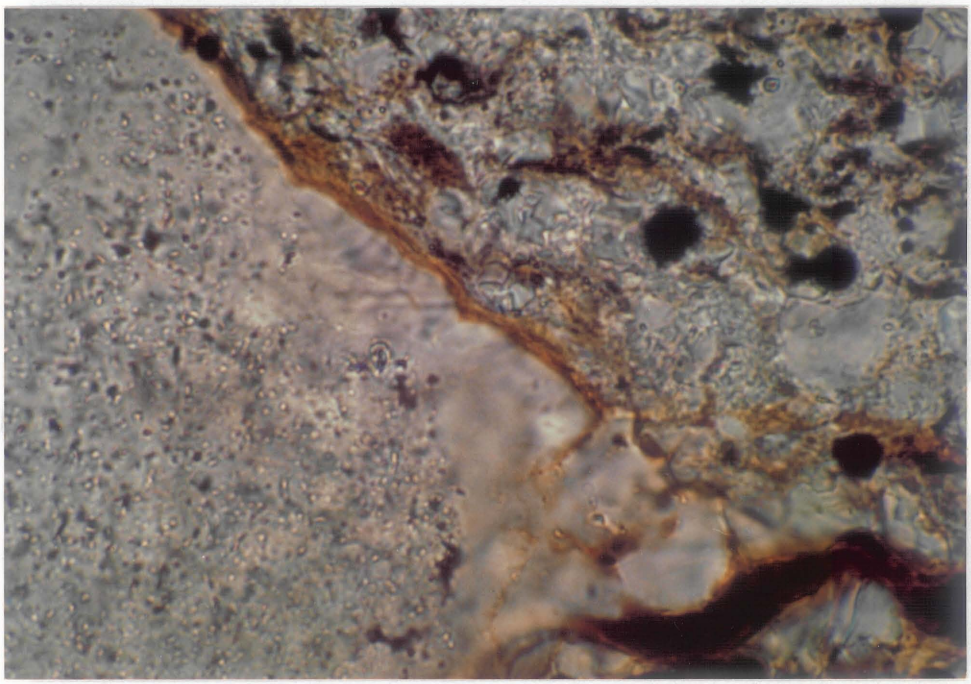
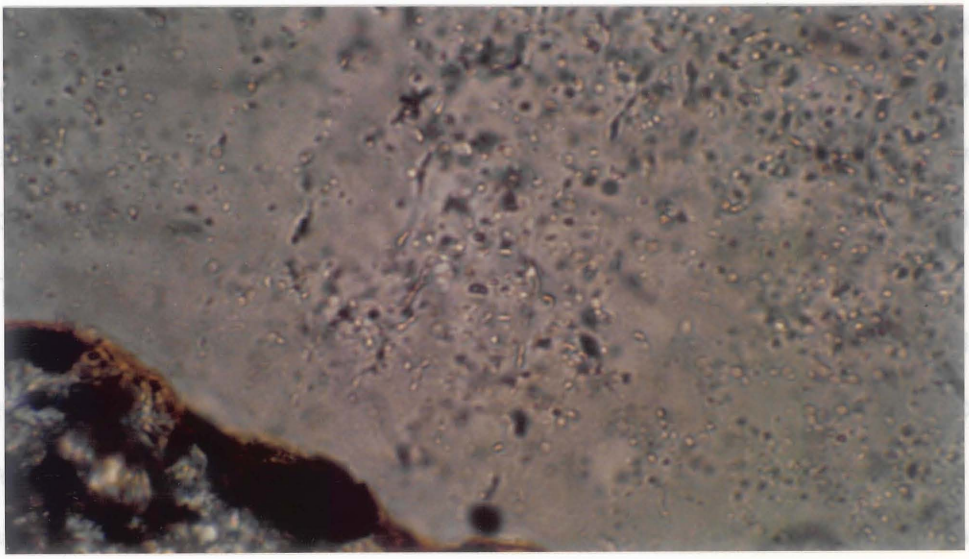
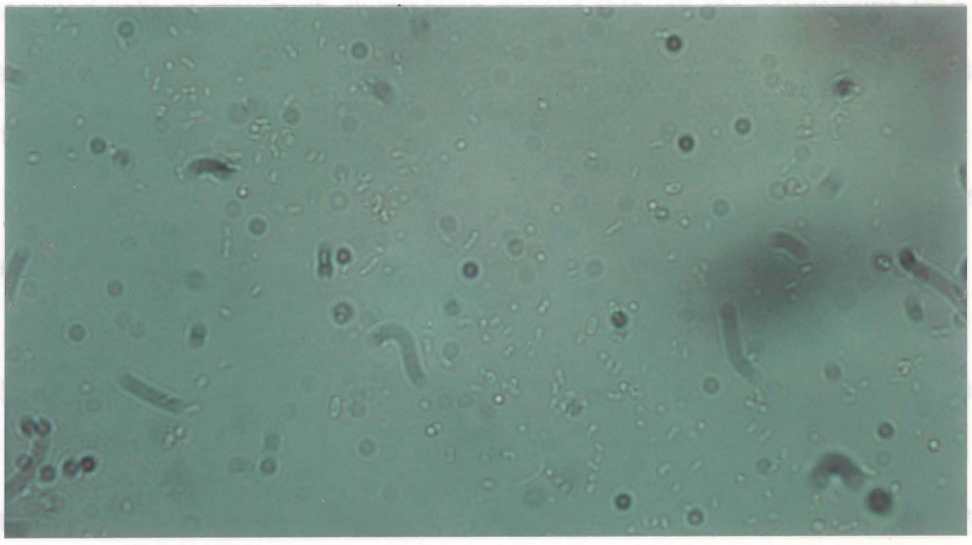


Figure 40. Fossil bacteria in the tip of the calcite cement illustrated in the preceeding figure. The lower left portion of the field of view shows a cloud of uniform, spherical fossil bacteria. The fossils are 1-2µm in diameter. Note the regular size and shape of the fossils, and that they are randomly distributed throughout the cement, not preferentialy incorporated along crystallographic axes.



A)



B)

Figure 41, A and B. A comparison of the morphology of fossil and living bacteria. (A) These fossil bacteria show well preserved chains of "rosaries" of bacterial bodies which closely resemble living filamentous marine bacteria. Magnification = 1,250 X. (B) A mixed culture of living marine bacteria in seawater. This photo was taken with the same microscope at the same magnification as in (A). Note the similar size and shape of individual living and fossil bacteria. Also note the similarity of the short chains and filamentous groupings between the living and fossil bacteria.

The bacterial fossils vary in density throughout individual cement blebs. Figure 40 illustrates a region of high density adjoining an area of low fossil density. The density of bacteria fossils varies substantially, as expected, between various cements. Some cements contain only rare bacteria, others preserve sparse clouds of and some contain dense populations of bacterial fossils.

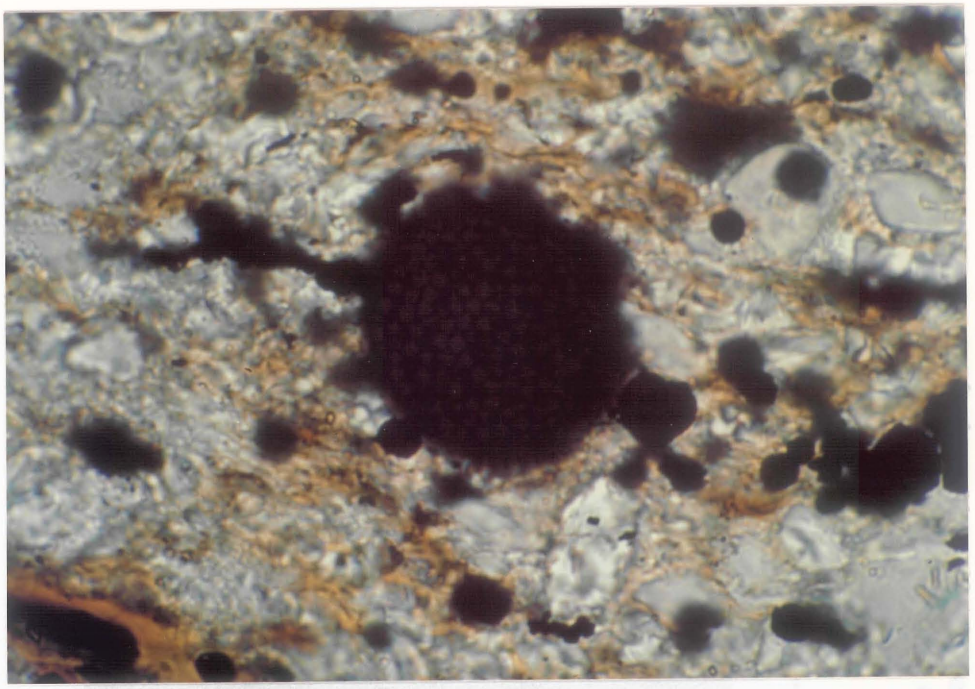
Becke Lines which surround clay flakes in the Schlacken obscure fossil bacteria. To determine if the clay-containing calcite cement between pyrite framboids held fossil bacteria, a modification of the White Card Technique was employed (Delgado,1977). A slip of ordinary white paper was placed below the stage and above the condensing lens of a standard petrographic microscope. Transmitted light at maximum illumination passes through the condensing lens and paper filter then through the sample thin section. The paper filters out optical interference produced by Becke Lines and amorphous organic matter (Figures 42A and B). The filter technique is most effective in analyzing thin sections less than thirty microns thick.

Petrographic observations on fosil bacteria were confirmed by study with an ISI 60A scanning electron microscope. Samples were first coated with carbon and then gold and grounded with graphite paint. SEM photos are presented that illustrate the shapes and distribution of the fossils within the void-filling cement of the concretionary layer (Figures 43-45).

Summary

Fossil bacteria occur in several morphologies in the calcite cement of the Schlacken. The bacterial fossils can be differentiated from inorganic fluid

B)



A)

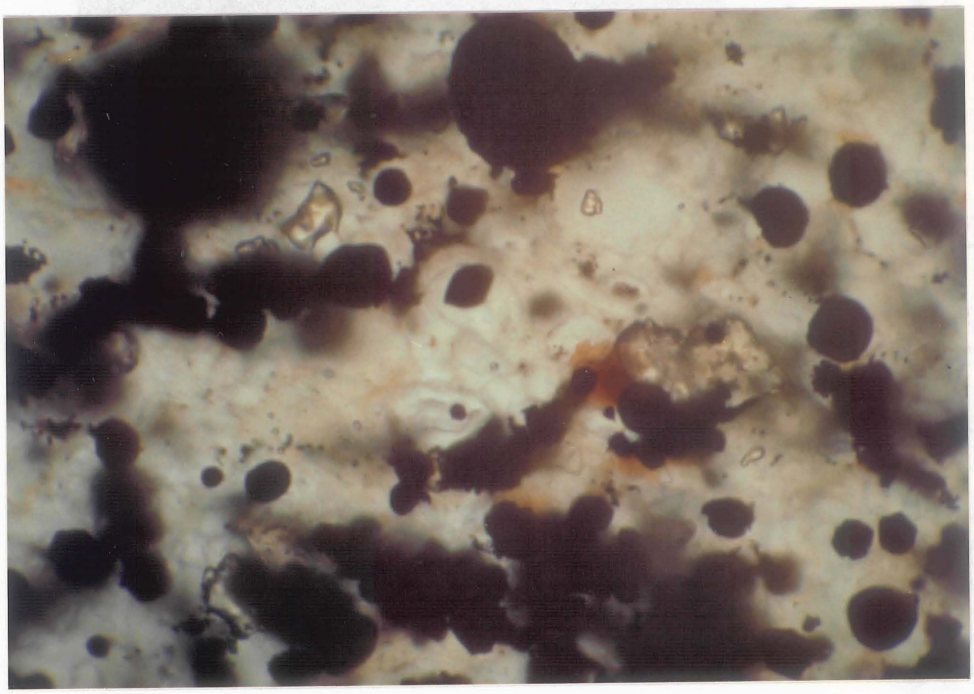


Figure 42, A and B. Comparison of normal transmitted light view (A) of a concretionary band with a "modified white card" filtered view (B). Optical interference from clay-flake Becke Lines and from amorphous organic matter obscure fossil bacteria in the unfiltered view. Fossil bacteria are revealed in the cement which outlines coccolith fragments in the filtered view.

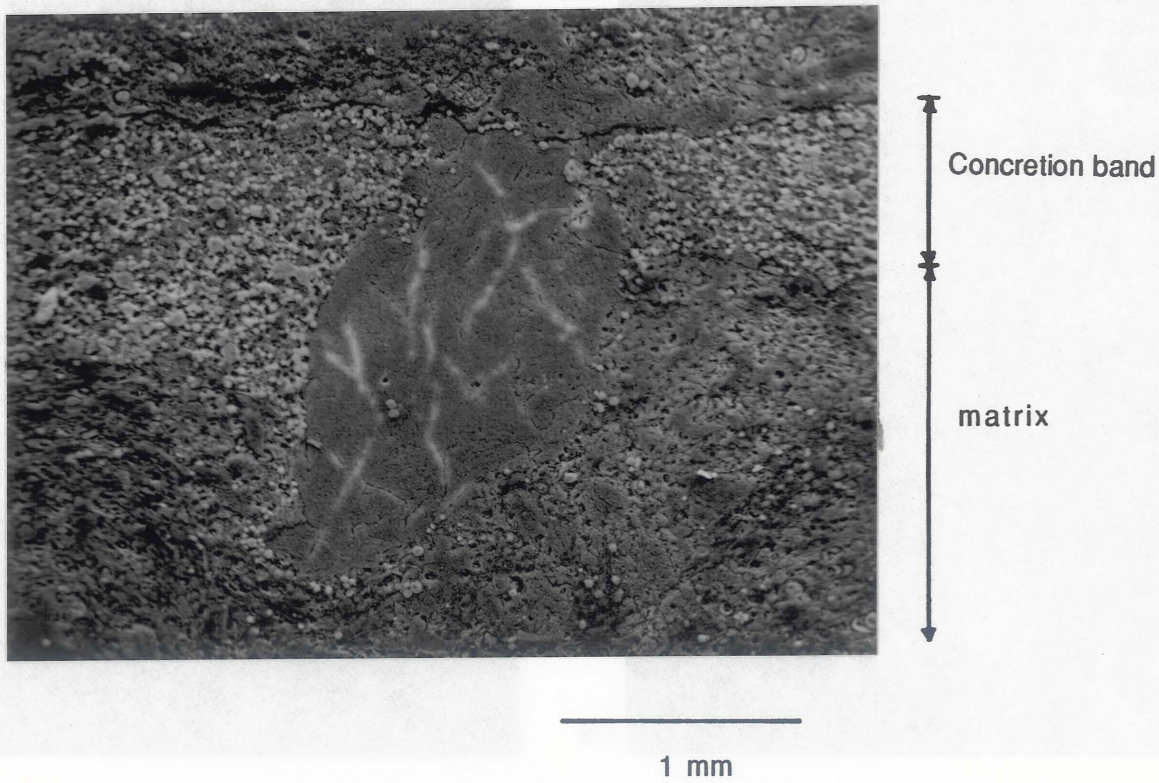


Figure 43. SEM image of an acetic acid etched thin section of the Schlacken. Central area is a void-filling calcite cement within the 1 mm thick concretionary band. This is the cement type that displays the most obvious fossil bacteria. Bacteria fossil on the surface of this calcite appear as one to two micron diameter spherical and rod-shaped holes. Magnification = 230 X. Scale bar = 1 mm.

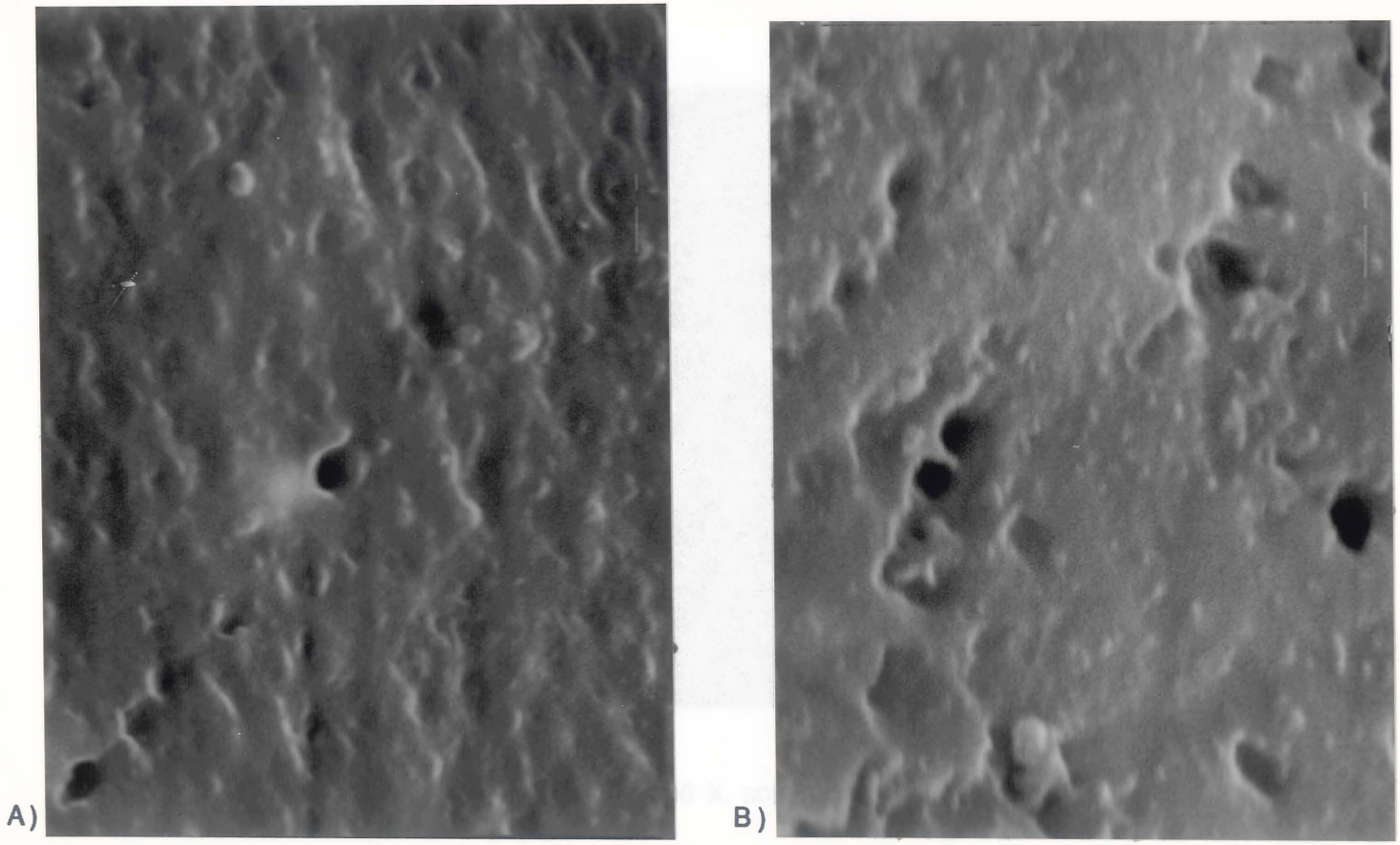
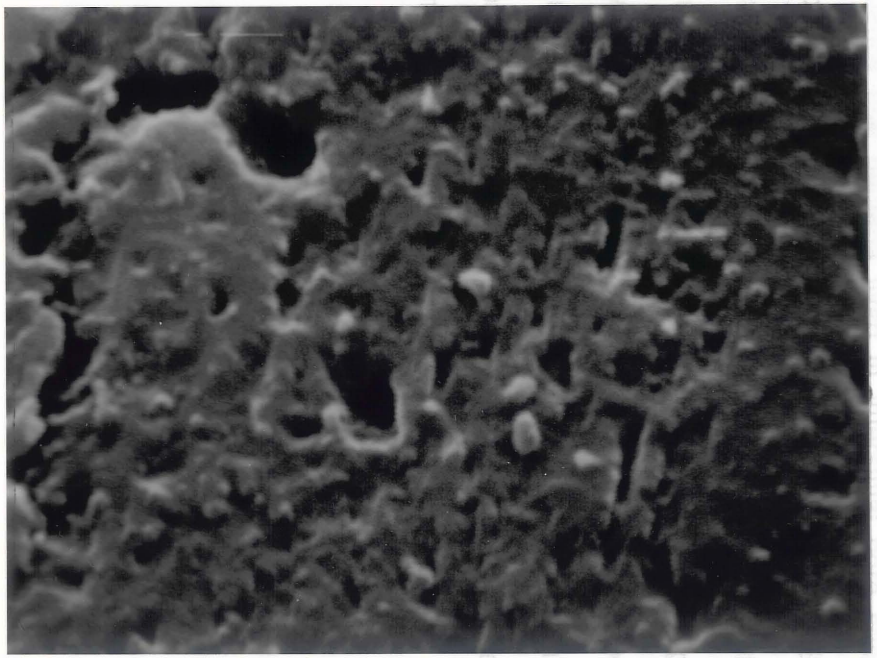


Figure 44. Two close-up views of the surface of the cement illustrated in the previous figure (43) before etching. (A) magnification = 6000X, scale bar = one micron. (B) magnification = 7,100 X, scale bar = one micron. Spherical, one micron diameter holes may be fossil molds of bacteria. These holes correlate well with the bacterial fossils identified in petrographic thin-section.



magnification = 7,100 X, scale bar = one micron.

Figure 45. SEM image of the calcite in Figure 43. The surface of the crystal has been etched with acetic acid. Note slight enlargement of one micron diameter holes. Compare these to the etch pits develped along crystallographic axes. The location of bacterial fossil molds are not controlled by crystallographic growth planes. The etch pits are angular and irregularly shaped, unlike the the rounded and regular bacteria fossil molds.

inclusions by their uniform size and shape, randem orientation in the calcite crystal structure, and their distinct resemblance to fossilized bacteria produced in laboratory experiments.

The preservation of bacterial fossils in calcite cement is direct physical evidence that bacteria lived in interstitial pore spaces and were entrapped in calcite during early diagenetic cementation of the Schlacken. The evidence of bacterial fossils combined with the preservation of authigenic minerals which were precipitated during early sulfidic diagenesis suggests that bacteria may have played an important role in the creation of local supersaturations of bicarbonate, hydrogen sulfide, and calcium ions. The precipitation of calcite was initiated within these geochemical microenvironments, and eventually cemented pores and framework grains to form the Schlacken.

Conclusions

The Bituminous Shale was deposited in a low-energy seaway well off the shore of a tropical, soil-producing source terrain located to the north and east. Pore waters of the ocean-floor mud were dysaerobic to anaerobic. Benthic waters were for the most part anaerobic to the sediment/water interface. Occasional oxygenation events allowed opportunistic benthic organisms to colonize the sea-floor. The aerobic/anaerobic boundary in the water column may have been located several millimeters above the sediment/water interface. The shells of benthic epibionts were preserved in-situ.

The diagenetic history of the Bituminous Shale was a uneventful and gradual process. Continuous dewatering and compaction gradually destroyed interstitial pore spaces. Sulfidic diagenesis produced first framboidal pyrite during open sediment/pore water conditions and later euhedral pyrite as the diffusion became restricted. Framboidal pyrite in the Bituminous Shale formed under anaerobic conditions. The sediment/pore water system was open enough to allow sulfate diffusion into the sediment and allow organic metabolic by-products and alkalinity produced during microbial sulfate reduction to escape. Euhedral pyrite formed later in diagenesis as communication between pores became restricted during sediment compaction.

The Bituminous Shales contain no petrographic evidence of Kauffman's proposed algal, fungal, or even bacterial mat. Evidence of intense bacterial activity during sulfidic diagenesis, however, is recorded in the microspar and other cements of the Schlacken.

The skeletal grains of the Schlacken formed as a winnowed lag deposit of Bituminous Shale sediments. During the early stages of sulfidic diagenesis the winnowed beds were rapidly cemented in a concretion-like sheet by microbially initiated precipitation of calcite.

Fossil bacteria discovered by modified petrographic techniques in the cements of the Schlacken are direct evidence of the presence and entrapment of bacteria during cementation, but do not conclusively prove their role in cement precipitation.

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